The present invention relates to a cationic electrodeposition coating composition comprising silica particles having pore volume of 0.44 to 1.8 ml/g and average particle size of no more than 10 μm, the composition showing square root of diffusion coefficient (√C) of no less than 2.5 upon diffusing a solution onto a coating film therewith; a cationic electrodeposition coating composition comprising silica particles having pore volume of 0.44 to 1.8 ml/g and average particle size of no more than 10 μm, wherein the composition shows minimum deposition pH of 11.90 to 12.00 during electrodeposition coating, and film resistance of 1,000 to 1,500 kΩ·cm² at film thickness of 15 μm and applied voltage of 240 V; and an article coated with such cationic electrodeposition coating composition. Therefore, the present invention can also provide a coating film formed with the cationic electrodeposition coating composition which can ensure higher corrosion resistance and higher throwing power in addition to other excellent coating properties, even if the resulting coating has extremely thin film thickness (e.g., about 7 μm).
Fig. 2

Electrodepositioning behavior during constant-current electrodeposition coating (1mA/cm²)

- Applied voltage (V)
- Conducting period (sec)

- Dielectric time
- Initiation of deposition
CATIONIC ELECTRODEPOSITION COATING COMPOSITION AND COATED ARTICLE THEREWITH

TECHNICAL FIELD

[0001] The present invention relates to a cationic electrodeposition coating composition, which especially provides a coating film having higher corrosion resistance even if the resulting coating is a considerably thin film, as well as an article coated with the composition.

BACKGROUND OF THE INVENTION

[0002] The electrodeposition coating is widely utilized as an undercoating method for an article, which has a large and complicated shape and needs coating having higher corrosion resistance, such as vehicle bodies, since the coating can be formed to detailed portions, even if the article has a complicated shape, and the coating can be provided automatically and continuously. The electrodeposition coating is also commonly available as an industrial coating method, since the electrodeposition coating has economical advantages and extremely higher efficiency on applying a coating composition in comparison with other coating methods. The cationic electrodeposition coating is carried out by immersing an article to be coated into a cationic electrodeposition coating composition as a cathode, and applying voltage.

[0003] Although the electrodeposition coating essentially has economical advantages and higher efficiency in applying a coating composition, as mentioned above, recently concepts based on resource conservation require much higher efficiency compared with that in the conventional methods even in the field of the electrodeposition coating. For example, thickness of the conventional coating film formed by the cationic electrodeposition coating method is approximately 20 μm, however, recently it is desirable that thickness of the surface coating film on the outer panel is approximately 15 μm.

[0004] Since thinner film allows more reduced amount of the coating composition to be used, the resource conservation can be theoretically established. Conventionally, thinner film could be readily obtained by shortening the period of the electrodeposition coating and/or reducing the electrical quantity to be applied during the electrodeposition coating. However, it is difficult to ensure corrosion resistance of the resulting coating film, especially for back of the article panel. Because thickness of the resulting back, i.e., inner, coating film on the article is also reduced after subsection of the article to the electrodeposition coating to obtain no more than 15 μm of outer, i.e., surface, film thickness. From this aspect, it can be seen that the key techniques providing a thinner outer surface coating and an adequate inner coating to the detailed portions, which coatings are both formed with the same composition having improved throwing power, and techniques improving corrosion resistance in the inner coated area (or thin layer area), wherein inner coated thin film has thickness of no more than 10 μm, particularly no more than 7 μm, are necessary.

[0005] JP-A-2003-268315 discloses a leadless cationic electrodeposition coating composition including silica particles having pore volume of 0.44 to 1.8 ml/g and average particle size of no more than 10 μm. The cationic electrodeposition coating composition is characterized in that the formed coating has a surface smoothing effect. However, it is not suggested in JP-A-2003-268315 that the coating, whose thickness is thin, for example, no more than 10 μm, particularly approximately 7 μm, has high corrosion resistance, and the composition has high throwing power.

[0006] JP-A-2004-269627 discloses a leadless cationic electrodeposition coating composition comprising an aqueous medium, and a binder resin, a neutralizing acid, an organic solvent, a pigment and a metal catalyst, which are dispersed or dissolved in the aqueous medium, is characterized in that the film resistance of an electrodeposition coating film on an article in 20 μm of thickness is 1,000 to 2,500 kΩ·cm², the electroconductivity of the coating composition is 1,500 to 2,000 μS/cm, and the minimum deposition pH in the electrodeposition coating is 11.90 to 12.00. In addition, JP-A-2004-269627 discloses that square root of diffusion coefficient is 2.5 to 3.2 upon diffusing a solution onto the coating film therewith (see claim 3). However, extremely thin film (e.g., thickness is about 7 μm), which is derived from the cationic electrodeposition coating composition, is not considered in JP-A-2004-269627.

SUMMARY OF THE INVENTION

[0007] The present invention consists in providing a cationic electrodeposition coating composition which can ensure higher corrosion resistance and higher throwing power in addition to other excellent coating properties, even if the resulting coating has extremely thin film thickness (e.g., about 7 μm).

[0008] Therefore, the present invention provides a cationic electrodeposition coating composition comprising silica particles having pore volume of 0.44 to 1.8 ml/g and average particle size of no more than 10 μm, the composition showing square root of diffusion coefficient (i.e., τ√ε) of no less than 2.5 upon diffusing a solution onto a coating film therewith, and a cationic electrodeposition coating composition comprising silica particles having pore volume of 0.44 to 1.8 ml/g and average particle size of no more than 10 μm, wherein the composition shows minimum deposition pH of 11.90 to 12.00 during electrodeposition coating, and film resistance of 1,000 to 1,500 kΩ·cm² at film thickness of 15 μm and applied voltage of 240 V, in order to solve the above described problems.

[0009] According to the preferable embodiment of the present invention, the cationic electrodeposition coating composition further comprises an amine modified epoxy resin (A) and a blocked isocyanate curing agent (B), wherein weight ratio of the amine modified epoxy resin (A) to the blocked isocyanate curing agent (B) is 50/50 to 90/10 (A/B), and the blocked isocyanate curing agent (B) comprises a blocked aliphatic polyisocyanate and a blocked aromatic polyisocyanate, wherein weight ratio of the blocked aliphatic polyisocyanate to the blocked aromatic polyisocyanate is 3/1 to 1/3 (the blocked aliphatic polyisocyanate/the blocked aromatic polyisocyanate).

[0010] In more preferable embodiment, content of the silica particles in the composition is 1 to 30% by weight relative to total weight of pigments.

[0011] Furthermore, the present invention provides an article coated with the cationic electrodeposition coating composition.
BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a schematic cross sectional diagram illustrating an embodiment of measuring system determining diffusion coefficient of a coating film, which includes coated article plate (100), coating film (101), silicone rubber packings (102) and (102), platinum ring electrode (103), Teflon® ring (104), article to be coated (105), electrometer (106), and recorder (107).

[0021] FIG. 2 is a graph illustrating correlation between applied voltage and conducting period for determining minimum deposition pH.

[0022] FIG. 3 is a schematic diagram illustrating an apparatus for measuring throwing power, which includes electrodeposition coating vessel (201), pipe (202), specimen plate (203), boundary (204), stirrer (205), power source (206), and electrodeposition coating composition (207).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0030] The present invention is described as follows in detail.

[0031] Generally, a cationic electrodeposition coating composition essentially comprises a cationic epoxy resin (particularly, an amine modified epoxy resin) and a curing agent for the resin (particularly, a blocked isocyanate curing agent), which are dispersed in an aqueous medium. In addition, pigments and/or other additives may be contained in the cationic electrodeposition coating composition in a dispersed state.

Silica Particles

[0032] As described above, the cationic electrodeposition coating composition according to the present invention is characterized in that the composition comprises certain silica particles. Silica particles are porous and have pore volume of 0.44 to 1.8 mL/g, preferably 0.8 to 1.6 mL/g. When silica particles have pore volume of less than 0.44 mL/g, it provides insufficient effect (i.e., poor corrosion resistance) of the coating film. When pore volume is further less than that value, this tendency is much more significant. When silica particles have pore volume of more than 1.6 mL/g, their dispersion stability is insufficient. When pore volume is further more than that value, their dispersion stability is significantly insufficient. Herein, "pore volume" means volume of pores in porous silica particles, i.e., porosity. Pore volume can be measured by mercury penetration method. Mercury penetration method includes allowing pores in a material (in a powder state) to be penetrated with mercury, and measuring pressure for the penetration and amount of penetrated mercury to determine specific surface and pore distribution. Mercury penetration type apparatus for pore distribution measurement can be employed to measure specific surface and pore distribution.

[0033] Silica particles have average particle size of no more than 10 μm, preferably 5 to 0.1 μm. When average particle size is less than 0.1 μm, it provides insufficient dispersion stability. When average particle size is more than 10 μm, it provides poor corrosion resistance. Herein, "average particle size" is generally used to represent a grain size of a particle (or represent if the particle size is large or small). For example, medium size corresponding to 50% by weight, arithmetical mean size, surface area mean size, volume-area mean size are used. Herein, "average particle size" is determined and represented by a laser method. Laser method includes dispersing particles in a solvent, irradiating laser beam on the dispersion, measuring the resulting scattering light, and computing to determine average particle size, particle size distribution, etc.

[0034] Although silica generally means solid material predominantly containing silicon dioxide, silica particles employed in the present invention are porous, as stated above, and should have pore volume of 0.44 to 1.8 mL/g and average particle size of no more than 10 μm. Silica particles having such properties are specially prepared, and therefore differ from well known silica gel and naturally occurring silica particles or clay (e.g., filler pigments such as kaolin). The silica particles employed in the present invention are prepared by mixing sodium silicate and an acid, that is so-called wet process. The specific silica particles employed in the present invention include SILYSLA which is commercially available from FUJI SILYSLA CHEMICAL LTD.

[0035] Generally, corrosion on a cathode allows pH around it to be alkaline to facilitate the corrosion. However, it is considered that presence of the silica particles in the composition provides pH buffering effect to prevent the alkallification, which can assert higher corrosion resistance of the resulting coating film.

[0036] It is considered that the silica particles employed in the present invention are in a solid state and may be a part of pigments which is described below. In this case, it is also considered that a part of the pigments may be replaced by the silica particles according to the present invention. Therefore, it is preferable that content of the silica particles is 1 to 30% by weight, more preferably 10 to 25% by weight relative to the total weight of the pigments. Addition of more than 30% of the silica particles provides poor smoothness of the resulting coating film. On the contrary, addition of less than 1% by weight of the silica particles provides their insufficient effect (i.e., poor corrosion resistance).

[0037] The leadless cationic electrodeposition coating composition according to the present invention contains a cationic epoxy resin and a curing agent in addition to the specific silica particles, as stated above, and may further optionally contain pigments and/or other additives. Hereinafter, individual components are described respectively.

Amine Modified Epoxy Resin

[0038] The amine modified epoxy resin employed in the present invention includes epoxy resins which modified by
amines. These amine modified epoxy resins may be known resins disclosed in JP-B-54-4978, JP-B-56-34186, etc.

[0039] The amine modified epoxy resin is typically produced by modifying all of epoxy group of a bisphenol type epoxy resin with an active hydrogen compound which can introduce a cationic group, or by modifying a part of epoxy groups with other active hydrogen compounds and modifying the residual epoxy groups with active hydrogen compounds which can introduce cationic groups.

[0040] The typical example of the bisphenol type epoxy resin is a bisphenol A type epoxy resin or a bisphenol F type epoxy resin. The commercially available product of the former includes Epikote 828 (manufactured by Yuka-Shell Epoxy Co., Ltd., epoxy equivalent: 180 to 190), Epikote 1001 (the same, epoxy equivalent: 450 to 500), Epikote 1010 (same, epoxy equivalent: 3000 to 4000) and the like, and the commercially available product of the latter includes Epikote 807 (same, epoxy equivalent: 170) and the like.

[0041] An epoxy resin containing an oxazolidone group, which has a structure disclosed in JP-A-5-306327 (see paragraph [0004]), can be employed as an amine modified epoxy resin, since the resulting coating film is to be superior in heat resistance and corrosion resistance.

[0042] As a method of introducing an oxazolidone group into an epoxy resin, for example, a blocked polyisocyanate which is blocked with lower alcohol such as methanol, and polyeopxide are heated in the presence of a basic catalyst to keep its temperature, and it is obtained by removing lower alcohol as a by-product with distillation from the system.

[0043] The preferable epoxy resin in particular is an epoxy resin containing an oxazolidone group. This is because coating film superior in heat resistance and corrosion resistance and further also superior in impact resistance is obtained.

[0044] It is known that the epoxy resin containing an oxazolidone group is obtained by reacting a bifunctional epoxy resin with a diisocyanate (namely, bisurethane) which is blocked with monoalcohol. For example, the specific example and production process of the epoxy resin containing an oxazolidone group are disclosed in Japanese Patent Publication No. 128959/2000, paragraphs 0012 to 0047.

[0045] These epoxy resins may be modified with appropriate resins (such as polyester polyol, polyether polyol, carboxyl acids and xylene resin) or mercaptol compounds. Furthermore, the epoxy resin can extend its chain utilizing the reaction of an epoxy group with diol or dicarboxylic acid.

[0046] It is desirable that the group in the epoxy resin is reacted with an active hydrogen compound so that an amine equivalent is 0.3 to 4.0 meq/g after ring opening and the primary amino group occupies more preferably 5 to 50% therein.

[0047] The active hydrogen compound capable of introducing the cationic group includes the acid salts of the primary amine, secondary amine and tertiary amine, sulfide and an acid mixture. The acid salts of primary amine, secondary amine or tertiary amine(s) are used as the active hydrogen compound capable of introducing the cationic group in order to prepare an epoxy resin containing primary amino, secondary amino or/and tertiary amino group(s) according to the present invention.

[0048] The specific examples include butylamine, octylamine, diethylamine, dibutylamine, methylbutylamine, monoethanolamine, diethanolamine, N-methylethanolamine, triethylamine hydrochloride, N,N-dimethylethanolamine acetate, a mixture of diethylsulfide and acetic acid and the like, additionally, the secondary amine blocking the primary amine such as the ketimine of amineethylethanolamine and the diketimine of diethyletherimine. A plural number of amines may be used in combination.

Sulfonium-modified Epoxy Resin

[0049] The cationic electrodeposition coating composition according to the present invention may include sulfonium-modified epoxy resins. The sulfonium-modified epoxy resins mean modified resins wherein an epoxy resin is modified with a sulfide compound and a neutralizing acid to form a sulfonium salt moiety upon opening the epoxy group on the resin. The sulfonium-modified epoxy resins may include resins which have been conventionally used and known to those skilled in the art (e.g., JP-A-6-128351, JP-A-7-206968, and the like). The sulfonium-modified epoxy resin can be typically produced by ring opening the epoxy group in a bisphenol type epoxy resin with a sulfide compound and a neutralizing acid.

[0050] The sulfide compound to be reacted with an epoxy resin includes all sulfide compounds, which can react with an epoxy group and have no reaction-interrupting group. The reaction between an epoxy resin and a sulfide compound must be proceeded in the presence of a neutralizing acid, so that a sulfonium group is introduced into the epoxy resin.

[0051] For example, sulfide compounds may include aliphatic sulfide, aliphatic and aromatic groups-containing sulfide, aralkyl sulfide or cyclic sulfide. Examples of the sulfide compounds to be used are diethyl sulfide, dipropyl sulfide, ethyl phenyl sulfide, tetramethylethylene sulfide, pentamethylene sulfide and the like.

[0052] Particularly preferable sulfide compound is a thiodialcohol represented by the formula:

\[ HO\cdot R \cdot S \cdot R' \cdot OH \]

wherein R and R' are each independently a straight or branched alkylenic group having 2 to 8 carbon atoms. Such sulfonium-modified epoxy resin allows establishment of film resistance to be delayed for instant after applying voltage during electrodeposition (about 10 seconds), and provides the binder resin with dispersion stability in water.

[0053] The thiodialcohol includes, for example, thioglycol, thiodipropanol, thiobutanol, 1-(2-hydroxyethylthio)-2-propanol, 1-(2-hydroxyethylthio)-2-propanediol, 1-(2-hydroxyethylthio)-2-butanol, 1-(2-hydroxyethylthio)-3-butoxy-1-propanol and the like. The most preferable sulfide compound is 1-(2-hydroxyethylthio)-2-propanol.

Blocked Polysiocyanate Curing Agent

[0054] The blocked isocyanate curing agent employed in the present invention preferably includes blocked polysiocyanate, which is prepared by blocking a polysiocyanate with a blocking agent, wherein the polysiocyanate means a compound having 2 or more of isocyanate groups in a
molecule. As the polyisocyanate, for example, any of an aliphatic type, an alicyclic type, an aromatic type, an aromatic-aliphatic type and the like may be used.

[0055] The specific example of the polyisocyanate includes tolylene diisocyanate (TDI), aromatic diisocyanates such as diphenylmethane diisocyanate (MDI), p-phenylene diisocyanate and naphthalene diisocyanate; aliphatic diisocyanates having a carbon number of 3 to 12 such as hexamethylene diisocyanate (HDI), 2,2,4-trimethylhexane diisocyanate and lysine diisocyanate; alicyclic diisocyanates having a carbon number of 5 to 18 such as 1,4-cyclohexane diisocyanate (CDI), isophorone diisocyanate (IPDI), 4,4'-dicyclohexylmethane diisocyanate (hydrogenated MDI), methylcyclohexane diisocyanate, isopropyldiene dicyclohexyl-4,4'-diisocyanate and 1,3-diisocyanatomethylcyclohexane (hydrogenated XDI), hydrogenated TDI and 2,5- or 2,6-his(isocyanatomethyl)-bicyclo[2,2,1]heptane (also called as norbornane diisocyanate); aliphatic diisocyanates having an aromatic ring, such as xylene diisocyanate (XDI) and tetramethylxylylene diisocyanate (TMDI); the modified product of these diisocyanates (urethanated product, carbodimides, urethondione, urethionime, biuret and/or isocyanurate modified product), etc. These can be used alone, or 2 or more thereof can be used in combination.

[0056] An adduct or a prepolymer which is obtained by reacting polyisocyanate with polyvalent alcohols such as ethylene glycol, propylene glycol, trimethylolpropane and hexanetriol at an NCO/OH ratio of 2 or more may be also used for the blocked isocyanate curing agent.

[0057] The polyisocyanate are preferably used in a combination of an aliphatic polyisocyanate and an aromatic polyisocyanate, since the resulting coating film is to be superior in smoothness and weather-resistance. Weight ratio of the aliphatic polyisocyanate to the aromatic polyisocyanate is 3/1 to 1/3, preferably 7/3 to 3/7 (aliphatic polyisocyanate/aromatic polyisocyanate (w/w)). When the weight ratio is more than 3/1, it provides poor smoothness in the coating film. When the weight ratio is less than 1/3, it provides poor weather-resistance in the coating film.

[0058] Preferable aliphatic polyisocyanates include, for example, hexamethylene diisocyanate, hydrogenated TDI, hydrogenated MDI, hydrogenated XDI, IPDI, norbornane diisocyanate, and dimer (biuret) and trimer (isocyanurate) thereof, and the like.

[0059] Preferable aromatic polyisocyanate include, for example, tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), xylene diisocyanate, and dimer, trimer and condensation product thereof, etc.

[0060] The blocking agent is added to a polyisocyanate, which is stable at ambient temperature, but can regenerate a free isocyanate group when it is heated to dissociation temperature or more.

[0061] In the case the curing process is carried out desirably at lower temperature (e.g., less than 160°C.), there can be used, as a blocking agent, lactam type blocking agents such as ε-caprolactam, δ-valerolactam, γ-butyrolactam and β-propiolactam, and oxime type blocking agents such as formaldoxime, acetaldoxime, acetoxime, methyl ethyl ketoxime, diacetyl monoxime and cyclohexane oxime.

[0062] Content of the binder resin containing an amine modified epoxy resin and a curing agent is generally 25 to 85% by weight, preferably 40 to 70% by weight relative to total solid contents of the electrodeposition coating composition.

Pigments

[0063] Typical electrodeposition coating composition generally contains a pigment as a coloring agent. The electrodeposition coating composition according to the present invention may also include pigments which have been conventionally used. The pigments include, for example, coloring pigments such as titanium oxide, carbon black and colochar; filler pigments such as kaoline, talc, aluminum silicate, calcium carbonate, mica and clay; anti-corrosion pigments such as zinc phosphate, iron phosphate, aluminum phosphate, calcium phosphate, zinc phosphate, zinc cyanide, zinc oxide, aluminum triplyloxophosphate, zinc molybdate, aluminum molybdate, calcium molybdate and aluminum phosphomolybdate and aluminum zinc phosphomolybdate, and the like.

[0064] Content of the pigments is generally 1 to 35% by weight, preferably 10 to 30% by weight relative to the total solid contents of the electrodeposition coating composition. As described above, it is considered that the specified silica particles employed in the present invention are a kind of solid components and can be a part of pigments. In this case, it is also considered that a part of the pigments may be replaced by the silica particles. In case where the silica particles can be considered as additives, content of the pigments is reduced to 0.01 to 15% by weight, preferably 0.2 to 2% by weight relative to the total solid contents in the electrodeposition coating composition.

[0065] It is preferable that the cationic electrodeposition coating composition according to the present invention is leadless in the environmental aspect. Accordingly, the composition should not contain anti-corrosion agents containing lead compounds, such as basic lead silicate, basic lead sulfate and minimum, nor anti-corrosion pigments containing lead compounds, such as lead cyanamide. Even if they are formulated, they should be used at lead ion concentration of no more than 100 ppm in the diluted coating composition (i.e., which is in a state ready to be poured in an electrodeposition coating bath). Higher lead ion concentration may contaminate the environment and prevent good smoothness of the resulting coating film.

Pigment Dispersed Paste

[0066] When a pigment is used as a component of the electrodeposition coating composition, the pigment is generally preliminarily dispersed in an aqueous medium with a resin, which is referred to as a pigment dispersion resin, at high concentration to form a paste shape. Since the pigment is powder, it is difficult to disperse the pigment by one step to a uniform low concentration state which is used for the electrodeposition coating composition. In general, the paste is referred to as a pigment dispersed paste.

[0067] The pigment dispersed paste is prepared by dispersing pigment(s) in an aqueous medium together with a pigment dispersion resin. In the preferable embodiment of the invention, pigments are combined with silica particles to prepare a pigment dispersed paste. As the pigment dispersion resin, there are generally used a cationic or nonionic low molecular weight surfactant and cationic polymers such as a modified epoxy resin having a quaternary ammonium groups and/or tertiary sulfonium groups. As the aqueous medium, ion-exchanged water, water containing a small amount of alcohols, and the like are used. Weight ratio of the
pigment dispersion resin to the pigment is generally 1:10 to 1:1 as basis of the solid contents (pigment dispersion resin: pigment (w/w)).

Electrodeposition Coating Composition

[0068] The electrodeposition coating composition according to the present invention can be prepared by dispersing an amine modified epoxy resin, a curing agent and a pigment dispersed paste containing silica particles in an aqueous medium. Generally, the aqueous medium includes a neutralizing agent to improve dispersibility of the amine modified epoxy resin. The neutralizing agents include inorganic acids and organic acids, such as hydrochloric acid, nitric acid, phosphoric acid, formic acid, acetic acid and lactic acid. The amount of the neutralizing agent to be used is an amount sufficient to achieve at least 20%, preferably 50 to 60% of neutralization ratio.

[0069] The amount of the curing agent to be used should be an amount sufficient to react with primary, secondary and/or tertiary amino groups or active hydrogen-containing functional groups such as hydroxyl groups in amine modified epoxy resins (or a sulfonium-modified epoxy resins) during curing process in order to provide a good cured coating film. Weight ratio of the amine modified epoxy resin (A) to the blocked polyisocyanate curing agent (B) is 50/50 to 90/10, preferably 55/45 to 80/20 (A/B (w/w)). When the weight ratio of the amine modified epoxy resin (A) to the blocked polyisocyanate curing agent (B) (A/B (w/w)) is less than 50/50, it provides poor smoothness of the coating film. When the weight ratio is more than 90/10, it provides insufficient corrosion resistance.

[0070] In the case that sulfonium-modified epoxy resin is combined with an cationic amine modified epoxy resin, mass ratio of the sulfonium-modified epoxy resin to the amine modified epoxy resin falls within a range of 10/90 to 50/50, preferably 25/75 to 50/50, more preferably 40/60 to 50/50. When the mass ratio is less than 10/90, it provides poor crater resistance (so-called gas-pinholes) of the resulting coating film. When the mass ratio is more than 50/50, it is difficult to improve the inadequate appearance of the resulting coating film.

[0071] The electrodeposition coating composition according to the present invention may include, as catalyst, organo tin compounds such as dibutyltin dilaurate, dibutyltin oxide, and urethane cleavage catalysts which have been conventionally used. Since these catalysts are substantially free from lead compounds, the amount of the catalyst to be used is preferably 0.1 to 5% by weight relative to the total amount of the blocked polyisocyanate compounds.

[0072] The electrodeposition coating composition may include additives which are conventionally used for coating compositions, such as water-compatible organic solvents, surfactants, antioxidants, UV absorbing agents and pigments.

[0073] The electrodeposition coating composition of the present invention is subjected to an electrodeposition coating wherein the composition is applied on an article to be coated to form a coating according to the methods well known to those skilled in the art. It is preferably that the article to be subjected to the electrodeposition coating and to be coated with the cationic electrodeposition coating composition is a conductor previously subjected to surface treatment such as zinc phosphate treatment by immersing or spraying methods, etc. Alternatively, surface of the article may be untreated. Herein, conductor means any material which can be a cathode upon electrodeposition coating and which is preferably, but is not limited to, metal substrate.

[0074] Such metal substrate may include steel plates such as cold-rolled steel plates and zinc-nickel steel plates. The steel plate may also be a construct so as to be used in the specified applications such as vehicle bodies as mentioned above. Herein, construct means the above listed metal substrate which has been subjected to, for example, press embossing to be formed into a convex-concave shape, so as to be used in the field of automobile production and other fields. It is preferable that the article to be coated is a construct made of zinc-nickel steel plate especially in the field of automobile production from the aspect of corrosion resistance.

[0075] Conditions for the electrodeposition are similar to those conventionally used in any electrodeposition coating. The applied voltage may be varied significantly in a range of 1 volt to a few hundreds volt. The current density is generally about 10 ampere/m² to 160 ampere/m². The current density tends to be decreased during electrodeposition.

[0076] After electrodeposition, the resulting coating film is subjected to a conventional baking process at elevated temperature, which includes baking in a stove or baking oven or under infrared heat lamp. Generally, the baking temperature may be varied in a range of about 140°C to about 180°C.

[0077] The electrodeposition coating composition according to the present invention must have minimum deposition pH of 11.90 to 12.00 during electrodeposition coating. When minimum deposition pH is less than 11.90, it provides poor stability of the composition in an electrodepositing coating bath. When minimum deposition pH is more than 12.00, it provides poor throwing power of the composition. Herein, minimum deposition pH means a calculated pH value based on necessary hydroxide ion concentration to deposit the binder resin in the cationic electrodeposition coating composition.

[0078] Value of minimum deposition pH can be determined by electrodepositing behavior during constant-current electrodeposition coating, i.e., electrodeposition coating at constant current density (mA/cm²). Once deposition of the resin contained in the electrodeposition composition is initiated on the surface of the article to be coated, the deposition increases electric resistance and accordingly demands higher voltage to be applied during constant-current electrodeposition coating (see FIG. 2). Herein, hydroxide ion concentration (C_{OH^—}) which is needed to deposit the resin can be determined from a conducting period until the electric resistance is increased, that is dielectric time, in accordance with the following formula:

\[ C_{OH^-} (\text{mmol/L}) = \frac{2 \times \text{current density (mA/cm}^2\text{)}}{v \times \text{(dielectric time (sec))}} \times F \times \text{z(D)} \]

wherein

\[ F \ (\text{Faraday constant}) = 96486.7 \]

\[ D \ (\text{diffusion coefficient of hydroxide ion [OH}]^-\text{)}) = 5 \times 10^{-5} \]

[0081] Minimum deposition pH can be determined according the following formula:

Minimum deposition pH = 14 - log_{10}(C_{OH^-})

[0082] Associated with the minimum deposition pH, FIG. 2 is a graph illustrating correlation between applied voltage and conducting period.
The electrodeposition process includes a step of immersing an article to be coated into a cationic electrodeposition coating composition, and a step of applying voltage between cathode which is said article and anode to deposit a coating film. Herein, the period for applying voltage depends on the electrodeposition conditions, but it may be generally 2 to 4 minutes. "Electrodeposited coating film" used herein means a coating film after the depositing process and prior to baking and curing process is described about that is an uncured coating film after electrodeposition coating.

Thickness of the electrodeposited coating film is preferably 5 to 30 µm, more preferably 7 to 25 µm. When the thickness of the electrodeposited coating film is less than 5 µm, it provides insufficient corrosion resistance. When the thickness is more than 30 µm, the coating composition is wasted. In the present invention, it is characterized that in the electrodeposition coating composition can provide a coating film having higher anti-corrosion property (i.e., corrosion resistance), as described above, even if its thickness decreases (e.g., about 7 µm), in comparison with the coating film formed with the conventional electrodeposition coating composition for thin-films, which has 10 µm of film thickness.

Furthermore, it is preferable to film resistance of the electrodeposited coating film to be 1000 to 1500 kΩ-cm² when film thickness is 15 µm and applied voltage is 240 V. When the film resistance of the electrodeposited coating film is less than 1000 kΩ-cm², it means insufficient electric resistance and provides poor throwing power. When the film resistance is more than 1500 kΩ-cm², it provides significantly poor appearance of the coating film. It is more preferably that the film resistance of the electrodeposited coating film is 1100 to 1200 kΩ-cm².

The film resistance of the electrodeposited coating film can be controlled by adjusting amount of charge transfer medium in the depositing film and viscosity thereof.

Followed by the electrodeposition process, thus obtained electrodeposited coating film is directly subjected, or after washing with water, to baking at 120 to 260 °C, preferably 140 to 220 °C, for 10 to 30 minutes to be cured. Herein, the coating film after baking and curing process is referred to as a "cured coating film".

Square root of diffusion coefficient (VTc) of the cured coating film formed with the cationic electrodeposition coating composition according to the present invention is no less than 2.5, preferably 2.5 to 3.2, more preferably 2.7 to 3.0. Herein, diffusion coefficient (TC) is an index indicating an extent of infiltration and diffusion of a solution into/into a cured coating film, which is a characteristic value associated with crosslinking density of the cured coating film. A cured coating film having higher crosslinking density, higher value of diffusion coefficient (TC) is provided.

Increased diffusion coefficient (TC) or increased crosslinking density of the cured coating film decreases diffusibility of electrolytes contained in mud or dirt, such as Na⁺, Cl⁻ and SO₄²⁻, into the cured coating film. Accordingly, it provides inhibited permeability of materials across the cured coating film, which materials are corrosive to the article to be coated. As a result, it enables such cured coating film to have an excellent effect preventing corrosion of the article, which is caused by adherence of mud or dirt.

Measurement of diffusion coefficient (TC) of a cured coating film is described below. Firstly, coated surface of an electrodeposited article plate is contacted with a solution. Secondary, voltage is applied between the plate and the solution at direct current. While time variation of electric resistance is measured, it can be seen that the electric resistance is significantly dropped. At this point, the solution is electrolyzed to give ions, and then these ions are attached to the surface of the coating film, penetrate through the coating film and diffused on the article. Herein, diffusion coefficient (TC) means period (min) from the point wherein voltage is applied to the point where electric resistance is dropped.

Method for measuring diffusion coefficient is disclosed in "SHIKIZAI" by Hitoshi Kawai, Takashi Yamamoto and Hiroshi Amagashita, 47 (1974). p.396, left column, line 24 from the bottom to p.398, left column, line 12. The description in this literature is incorporated herein by reference.

In the present invention, zinc steel plate is used as an article to be coated for measuring diffusion coefficient. As a specimen plate, a coated plate is prepared by electrodeposition coating composition on the zinc plate with 7 µm of coating thickness, and then dried at 150 °C for 25 minutes. As the contacting solution, a combined solution (water/methanol=½ (v/v)) is used.

FIG. 1 illustrates a measuring apparatus including platinum ring electrode (103) and Teflon® ring (104) which are placed on coating film (101) of coated article plate (100), and silicone rubber packings (102) and (102) set on the both sides of the electrode (103). The apparatus is put into a constant air temperature oven, and then the temperature is adjusted to 28 °C in accuracy within ±0.1 °C.

Voltage is applied between article to be coated (105) and platinum ring electrode (103) at direct current. The solution (water/methanol=½ (v/v)) was poured into the ring (104). Once the solution is poured, time variation of current is measured by 610 °C. electrometer (106) manufactured by Keithley Instruments Inc., and recorded on recorder (107). Surface temperature of the coated article plate can be measured by copper-constantan thermoelement (PHILIPS, PR6452A) (non-indication), which is attached on the plate.

A graph is prepared, wherein specific resistance (Ω·cm) of the coating film is plotted relative to time (min). On the graph, TC (min) is corresponding to the point where slope is initially changed.

According to the present invention, the cationic electrodeposition coating composition contains silica particles having specified structures, and the formed coating film thereof has controlled diffusion coefficient, which can provide anti-corrosion property (i.e., corrosion resistance), even if the coating film has significantly degreased thickness compared with the conventional coating film (e.g., thickness is about 7 µm), as well as improved surface smoothness of the coating film. Furthermore, control of minimum deposition pH of the present cationic electrodeposition coating composition containing the certain silica particles as well as control of film resistance of the electrodeposited coating film, when the applied voltage is 240 V and the coating thickness is 15 µm, during the electrodepositing procedure,
can provide higher throwing power in addition to anti-corrosion property (i.e., corrosion resistance) and improved surface smoothness of the coating film, even if the coating film has significantly degraded thickness compared with the conventional coating film (e.g., thickness is about 7 μm). The cationic electrodeposition coating composition according to the present invention can also provide excellent corrosion resistance on zinc steel plate approved by humidity cabinet test and wet-dry cycle test.

EXAMPLES

[0097] The present invention is further described below according to Preparation Examples and Examples in only way of exemplification, but the present invention is not limited to these examples. In the Preparation Examples and Examples, “part(s)” and “%” are according to weight basis unless otherwise noted.

Example A

Preparation Example A1

Synthesis of Amine Modified Epoxy Resin

[0998] In a flask equipped with a stirrer, a cooling tube, a nitrogen introducing tube, a thermometer and a dropping funnel, 752.0 parts of bisphenol A type epoxy resin (epoxy equivalent: 188), 77.0 parts of methanol, 200.3 parts of methyl isobutyl ketone and 0.3 part of dibutyltin dilaurate were weighted. The mixture was stirred at room temperature to form a homogeneous solution. Dropwise addition of 174.2 parts of mixture of 2,4- and 2,6-tolylidenediisocyanates (2,4-form/2,6-form =80/20 as basis of mass ratio) over 50 minutes raised temperature in the system to 70° C. due to exothermic heat. IR spectrum indicated disappearance of absorption peak at 2280 cm⁻¹ identified with the isocyanate group and appearance of absorption peak at 1730 cm⁻¹ identified with the carbonyl group in the urethane.

[0999] 2.7 Parts of N,N-dimethylbenzylamine were added to the reaction mixture, and then temperature in the reaction system was raised to 120° C. The reaction was continued until the epoxy equivalent reached to 463 with removing methanol as a by-product with a decantar. IR spectrum indicated disappearance of absorption peak at 1730 cm⁻¹ identified with the carbonyl group in the urethane and appearance of absorption peak at 1750 cm⁻¹ identified with the carbonyl group in the oxazolidone ring.

[0100] 158.3 Parts of octyllic acid and 83.3 parts of methyl isobutyl ketone were added to the reaction mixture and the reaction was continued until the epoxy equivalent reached to 1146 with the temperature kept at 125° C. Cooling was continued until the temperature in the reaction system decreased to 110° C. 47.2 Parts of ketamine of aminomethyl ethanolaminolime (in 79% by mass of methyl isobutyl ketone solution), 42.0 parts of diethanolamine, 30.0 parts of N-methylenehexanolamine and 17.3 parts of methyl isobutyl ketone were added to the reaction mixture, and then the temperature was raised to 120° C. The reaction was continued for 2 hours at the same temperature to yield an amino group-containing epoxy resin containing 80% of nonvolatile contents.

Preparation Example A2

Synthesis of Blocked Aliphatic Polyisocyanate Curing Agent

[0101] In a flask equipped with a stirrer, a cooling tube, a nitrogen introducing tube, a thermometer and a dropping funnel, 199 parts of isocyanurate-type trimer of hexamethylenediamine isocyanates (CORONATE HX manufactured by NIPPON POLYURETHANE INDUSTRY CO., LTD.), 122.8 parts of methyl isobutyl ketone and 0.2 part of dibutyltin dilaurate were weighted and heated to 50° C. 87 Parts of methyl ethyl ketone oxime were added dropwise over 2 hours with the temperature kept at 50° C. with externally cooling. Followed by the addition, the temperature was raised to 70° C. The reaction was continued with the temperature kept at the same until IR analysis indicated consumption of the isocyanate group to give an aliphatic blocked polyisocyanate curing agent.

Preparation Example A3

Synthesis of Blocked Aromatic Polyisocyanate Curing Agent

[0102] In a flask similar to that in the Preparation Example A1, 723 parts of diphenylmethane-4,4'-diisocyanate, 350 parts of methyl isobutyl ketone (MIBK) and 0.01 part of dibutyltin dilaurate were weighted. The resulting reaction mixture was heated to 70° C. and homogeneously dissolved. 131 Parts of x-caprolactam was dissolved in 546 parts of butyl cellosolve. The solution was added dropwise over 2 hours. Followed by the addition, the reaction was continued with the reaction temperature kept at 90° C. until absorption peak identified with the isocyanate group was disappeared on IR spectrum measurement to give a blocked aromatic polyisocyanate curing agent (resin solid contents: 80%).

Preparation Example A4

Preparation of Pigment Dispersion Resin

[0103] 222.0 Parts of isophorone diisocyanate (hereinafter abbreviated as IPDI) were added into a reaction vessel equipped with a stirrer, a cooling tube, a nitrogen introducing tube and a thermometer. 39.1 Parts of MIBK were added to dilute, and then 0.2 part of dibutyltin dilaurate was added to the mixture. Subsequently, temperature was raised to 50° C. and 131.5 parts of 2-ethylhexanol were added dropwise over 2 hours under dried nitrogen atmosphere with stirring. The reaction temperature was kept at 50° C. with suitable cooling to give a 2-ethylhexanol-halfblocked IPDI.

[0104] Subsequently, 376.0 parts of Epikote 828 (bisphenol A type epoxy resin manufactured by Yuka-Shell Epoxy Co., Ltd., epoxy equivalent: 182 to 194), 114.0 parts of bisphenol A and 29.2 parts of octyllic acid were weighted in a reaction vessel equipped with a stirrer, a cooling tube, a nitrogen introducing tube and a thermometer. The reaction mixture was heated to 130° C. under nitrogen atmosphere. 0.15 Part of dimethylbenzylamine was added to the mixture. The exothermic reaction was maintained at 170° C. for 1 hour to give a bisphenol A type epoxy resin (epoxy equivalent: 649).

[0105] Subsequently, the reaction system was cooled to 40° C. 396.8 Parts of 2-ethylhexanol-halfblocked IPDI as prepared above was added to the reaction mixture. The
reaction was maintained at 140°C for 1 hour. Subsequently, 323.2 parts of ethyleneglycol monobutyl ether were added to dilute the mixture. The reaction mixture was cooled to 100°C, and then 188.8 parts of 78.3% MIBK solution containing methyl isobutyl mono-ketimine compound of aminoethyl ethanolamine were added.

**[0106]** The mixture was maintained at 110°C for 1 hour, and then cooled to 90°C, thereto 360.0 parts of ion-exchange water were added. The reaction system was maintained with stirring for further 30 minutes to convert the ketimine moieties in the epoxy resin to the corresponding primary amino groups. Excess amount of water and MIBK were removed from the mixture in vacuo. Dilution with 588.1 parts of ethyleneglycol monobutyl ether gave a primary amino group-containing pigment dispersion resin (resin solid contents: 50%).

Preparation Example A5

Preparation of Pigment Dispersed Paste

**[0107]** 60 Parts of the pigment dispersion resin prepared in the Preparation Example A4 (as basis of solid contents), 100.0 parts of pigments listed on Table 1 and 221.7 parts of ion-exchange water were put into a sand-grinding mill in order to disperse pigments at no more than 10 μm of particle size to give a pigment dispersed paste (Paste AA to AG).

| TABLE 1-continued |
| Composition |
| No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | No. 6 | No. 7 |
| Paste dispersed paste |
| Paste AA | Paste AC | Paste AE | Paste AF | Paste AD | Paste AE | Paste AG |
| A1 | A2 | A3 | A1 | A2 | A3 | A4 |
| Carbon black | 2 | 2 | 2 | 2 | 2 | 2 |
| Titanium | 48 | 48 | 48 | 48 | 48 | 48 |
| Calcined kaolin | 30 | 40 | 20 | 50 | 50 | 50 |
| Silica particles A | 20 | 0 | 30 | 0 | 0 | 0 |
| Silica particles B | 0 | 10 | 0 | 0 | 0 | 0 |
| Silica particles C | 0.8 ml/g. | Average particle size: 2.5 μm |
| Silica particles C | 0 | 25 | 0 | 0 | 0 | 0 |
| Silica particles C | 0.44 ml/g. | Average particle size: 6.5 μm |
| Content of silica compound in pigments | 20 | 10 | 30 | 0 | 0 | 0 |

[Ex. A] Composition of 2O10 30 O O 2O silica compound in pigments manufactured by FUJISILYSIACHEMICAL LTD. *Silica particles: SYLYSIA 770 manufactured by FUJISILYSIACHEMICAL LTD.

Example A1

**[0108]** An amine modified epoxy resin of Preparation Example A1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example A2 and the polyisocyanate curing agent of Preparation Example A3 (weight ratio of the agents, Preparation Example A2/Preparation Example A3 = 1/1)) were homogeneously mixed (resin : curing agent = 60:40 as basis of solid contents). 3% Ethyleneglycol mono-2-ethylhexyl ether was added relative to the solid contents of the mixture. 90% acetic acid was added to the mixture to achieve 43.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1500.0 Parts of the main emulsion and 541.7 parts of the pigment dispersed paste AA prepared in the Preparation Example A5 by using the pigment dispersion resin prepared in the Preparation Example A4 were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide to give a cationic electrodeposition coating composition (solid contents: 20.0%).

**[0109]** Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 μm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Results are shown in Table 2.

Example A2

**[0110]** An amine modified epoxy resin of Preparation Example A1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example A2 and the polyisocyanate curing agent of Preparation Example A3 (weight ratio of the agents, Preparation Example A2/Preparation Example A3 = 1/3)) were homogeneously mixed (resin : curing agent = 80:20 as basis of solid contents). 3% Ethyleneglycol mono-2-ethylhexyl ether was added relative to the solid contents of the mixture. 90% acetic acid was added to the mixture to achieve 43.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1500.0 Parts of the
main emulsion and 541.7 parts of the pigment dispersed paste A8 prepared in the Preparation Example A5 by using the pigment dispersion resin prepared in the Preparation Example A4 were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide to give a cationic electrodeposition coating composition (solid contents: 20.0%).

[0111] Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 μm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Results are shown in Table 2.

Example A3

[0112] An amine modified epoxy resin of Preparation Example A1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example A2 and the polyisocyanate curing agent of Preparation Example A3 (weight ratio of the agents, Preparation Example A2/Preparation Example A3=3/1)) were homogeneously mixed (resin : curing agent=50:50 as basis of solid contents). 3% Ethyleneglycol mono-2-ethylhexyl ether was added relative to the solid contents of the mixture. 90% acetic acid was added to the mixture to achieve 43.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1500.0 Parts of the main emulsion and 541.7 parts of the pigment dispersed paste AC prepared in the Preparation Example A5 by using the pigment dispersion resin prepared in the Preparation Example A4 were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide to give a cationic electrodeposition coating composition (solid contents: 20.0%).

[0113] Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 μm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Results are shown in Table 2.

Comparative Example A1

[0114] An amine modified epoxy resin of Preparation Example A1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example A2 and the polyisocyanate curing agent of Preparation Example A3 (weight ratio of the agents, Preparation Example A2/Preparation Example A3=9/1)) were homogeneously mixed (resin : curing agent=80:20 as basis of solid contents). 3% Ethyleneglycol mono-2-ethylhexyl ether was added relative to the solid contents of the mixture. 90% acetic acid was added to the mixture to achieve 43.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1500.0 Parts of the main emulsion and 541.7 parts of the pigment dispersed paste AD prepared in the Preparation Example A5 by using the pigment dispersion resin prepared in the Preparation Example A4 were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide to give a cationic electrodeposition coating composition (solid contents: 20.0%).

[0115] Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 10 μm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Results are shown in Table 2.

Comparative Example A2

[0116] The cationic electrodeposition coating composition prepared in the Comparative Example A1 was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 μm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Results are shown in Table 2.

Comparative Example A3

[0117] An amine modified epoxy resin of Preparation Example A1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example A2 and the polyisocyanate curing agent of Preparation Example A3 (weight ratio of the agents, Preparation Example A2/Preparation Example A3=1/1)) were homogeneously mixed (resin : curing agent=60:40 as basis of solid contents). 3% Ethyleneglycol mono-2-ethylhexyl ether was added relative to the solid contents of the mixture. 90% acetic acid was added to the mixture to achieve 43.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1500.0 Parts of the main emulsion and 541.7 parts of the pigment dispersed paste A9 prepared in the Preparation Example A5 by using the pigment dispersion resin prepared in the Preparation Example A4 were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide to give a cationic electrodeposition coating composition (solid contents: 20.0%).

[0118] Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 μm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Results are shown in Table 2.

Comparative Example A4

[0119] An amine modified epoxy resin of Preparation Example A1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example A2 and the polyisocyanate curing agent of Preparation Example A3 (weight ratio of the agents, Preparation Example A2/Preparation Example A3=9/1)) were homogeneously mixed (resin : curing agent=95:5 as basis of solid contents). 3% Ethyleneglycol mono-2-ethylhexyl ether was added relative to the solid contents of the mixture. 90% acetic acid was added to the mixture to achieve 43.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1500.0 Parts of the main emulsion and 541.7 parts of the pigment dispersed paste AG prepared in the Preparation Example A5 by using the pigment dispersion resin prepared in the Preparation Example A4 were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide to give a cationic electrodeposition coating composition (solid contents: 20.0%).
Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 µm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Results are shown in Table 2.

The electrodeposited coating films and cured coating films thereof were prepared with the cationic electrodeposition coating compositions which had been obtained in the Examples and Comparative Examples were each evaluated by the following methods.

Diffusion coefficient

Diffusion coefficient was measured by using a steel plate which had been treated with zinc phosphate (wherein SURFDINE SD-2500 treatment defined in JIS G 3141 SPCC-SD was employed) in accordance with the method described above. Note that it is represented by square root of diffusion coefficient (i.e., V*G) in the following Table 2.

Corrosion resistance

Corrosion resistance was evaluated by using cyclemode disclosed in JP-A-2001-294816. Valuation basis is as follows.

- : No more than 30% of blister occurring area after 120 cycles
- : No more than 50% of blister occurring area after 120 cycles
X : No more than 80% of blister occurring area after 120 cycles
XX : No less than 80% of blister occurring area after 120 cycles

### TABLE 2

<table>
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</thead>
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<td>A2</td>
<td>A3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Combined silica species</td>
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<td>B</td>
<td>C</td>
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<td>Pore volume</td>
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<tr>
<td>Diffusion coefficient (<em>V</em>G)</td>
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<td>2.9</td>
<td>2.5</td>
<td>1.5</td>
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<td>Amine modified epoxy resin (A)/Curing agent (B)</td>
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<td>50/50</td>
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<td>1/3</td>
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<tr>
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<td>1/1</td>
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<tr>
<td>Corrosion resistance</td>
<td>☺</td>
<td>☺</td>
<td>☺</td>
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</tr>
</tbody>
</table>

EXAMPE B

**Preparation Example B**

**Synthesis of Amine Modified Epoxy Resin**

In a flask equipped with a stirrer, a cooling tube, a nitrogen introducing tube, a thermometer and a dropping funnel, 752.0 parts of bisphenol A type epoxy resin (epoxy equivalent: 188), 77.0 parts of methanol, 200.3 parts of methyl isobutyl ketone and 0.3 part of dibutyltin dilaurate were weighted. The mixture was stirred at room temperature to form a homogeneous solution. Dropwise addition of 174.2 parts of mixture of 2,4- and 2,6-tolylene diisocyanates (2-form/2,6-form=80/20 as basis of mass ratio) over 50 minutes raised temperature in the system to 70°C. due to exothermic heat. IR spectrum indicated disappearance of absorption peak at 2280 cm⁻¹ identified with the isocyanate group and appearance of absorption peak at 1730 cm⁻¹ identified with the carbonyl group in the urethane.

2.7 Parts of N,N-dimethylbenzylamine were added to the reaction mixture, and then temperature in the reaction system was raised to 120°C. The reaction was continued until the epoxy equivalent reached to 463 with removing methanol as a by-product with a decanter. IR spectrum indicated disappearance of absorption peak at 1730 cm⁻¹ identified with the carbonyl group in the urethane and appearance of absorption peak at 1750 cm⁻¹ identified with the carbonyl group in the oxazolidone ring.

158.3 Parts of octyl acid and 83.3 parts of methyl isobutyl ketone were added to the reaction mixture and the reaction was continued until the epoxy equivalent reached to 1146 with the temperature kept at 125°C. Cooling was continued until the temperature in the reaction system
decreased to 110° C. 47.2 Parts of ketimine of aminoethyl ethanolamine (in 79% by mass of methyl isobutyl ketone solution), 42.0 parts of diethanolamine, 30.0 parts of N-methyllethanolamine and 17.3 parts of methyl isobutyl ketone were added to the reaction mixture, and then the temperature was raised to 120° C. The reaction was continued for 2 hours at the same temperature to yield an amino group-containing epoxy resin containing 80% of nonvolatile contents.

Preparation Example B2
Synthesis of Blocked Aliphatic Polyisocyanate Curing Agent

[0131] In a flask equipped with a stirrer, a cooling tube, a nitrogen introducing tube, a thermometer and a dropping funnel, 199 parts of isocyanurate-type trimer of hexamethylenediisocyanates (CORONATE HX manufactured by NIPPON POLYURETHANE INDUSTRY CO., LTD.), 122.8 parts of methyl isobutyl ketone and 0.2 part of dibutyltin dilaurate were weighted and heated to 50° C. 87 Parts of methyl ethyl ketone oxide were added dropwise over 2 hours with the temperature kept at 50° C. with externally cooling. Followed by the addition, the temperature was raised to 70° C. The reaction was continued with the temperature kept at the same until IR analysis indicated consumption of the isocyanate group to give an aliphatic blocked polyisocyanate curing agent.

Preparation Example B3
Synthesis of Blocked Aromatic Polyisocyanate Curing Agent

[0132] In a flask similar to that in the Preparation Example B1, 723 parts of diphenylmethane-4,4′-diisocyanate, 350 parts of methyl isobutyl ketone (MIBK) and 0.01 part of dibutyltin dilaurate were weighted. The resulting reaction mixture was heated to 70° C. and homogeneously dissolved. 131 Parts of 1-carboxylactam was dissolved in 546 parts of butyl cellosolve. The solution was added dropwise over 2 hours. Followed by the addition, the reaction was continued with the reaction temperature kept at 90° C. until absorption peak identified with the isocyanate groups was disappeared on IR spectrum measurement to give a blocked aromatic polyisocyanate curing agent (resin solid contents: 80%).

Preparation Example B4
Preparation of Sulfonium-modified Epoxy Resin Emulsion

[0133] In a flask equipped with a stirrer, a cooling tube, a nitrogen introducing tube, a thermometer and a dropping funnel, 87 parts of 2,4- and 2,6-tolyleneisocyanates (mass ratio=8:2), 85 parts of MI BK and 0.1 part of dibutyltin dilaurate were weighted. 52 Parts of methanol were added dropwise with stirring the reaction mixture. The reaction took place at room temperature. The reaction temperature was raised to 60° C. due to exothermic heat. The reaction was predominantly maintained in a range of 60 to 65° C. until absorption peak identified with isocyanate groups was disappeared with IR spectrum measurement.

[0134] Subsequently, 550 parts of epoxy resin (epoxy equivalent: 188), which had been prepared from bisphenol A and epichlorohydrin according to the known method, were added to the reaction mixture and the mixture was heated to 125° C. Subsequently, 1.0 Part of benzyltrimethylamine was added to the mixture. The reaction was continued at 130° C. to give epoxy equivalent of 330.

[0135] Subsequently, 100 parts of bisphenol A and 36 parts of acetic acid were added to the reaction mixture. The reaction was maintained at 120° C. to give epoxy equivalent of 1030. Subsequently, 107 parts of MI BK were added to the reaction mixture. The reaction mixture was cooled. 52 Parts of SII-100 (1-(2-hydroxyethylthio)-2-propanol manufactured by Sanyo Chemical Industries, Ltd.), 21 parts of ion-exchange water, 39 parts of 88% lactic acid were added to the mixture. The reaction was maintained at 80° C. The reaction was continued until acid value was less than 5 to give a tertiary sulfonium salt group-containing epoxy resin (resin solid contents: 80%).

[0136] The resulting resin and the blocked isocyanate curing agent prepared in the Preparation Example B2 were homogeneously combined (the resin/the blocked isocyanate curing agent=60/40 (as basis of solid content)). Subsequently, ion-exchange water was added slowly to dilute the mixture. MI BK was removed in vacuo to give a blocked isocyanate-containing sulfonium-modified epoxy resin emulsion (solid contents: 30%). Milliequivalent of base corresponding to 100 g of resin solid contents in the emulsion was 10.

Preparation Example B5
Preparation of Pigment Dispersion Resin

[0137] 222.0 Parts of isophorone diisocyanate (hereinafter abbreviated as IPDI) were added into a reaction vessel equipped with a stirrer, a cooling tube, a nitrogen introducing tube and a thermometer. 39.1 Parts of MI BK were added to dilute, and then 0.2 part of dibutyltin dilaurate was added to the mixture. Subsequently, temperature was raised to 50° C. and 131.5 parts of 2-ethylhexanol were added dropwise over 2 hours under dried nitrogen atmosphere with stirring. The reaction temperature was kept at 50° C. with suitable cooling to give 2-ethylhexanol-halfblocked IPDI.

[0138] Subsequently, 376.0 parts of Epikote 828 (bisphenol A type epoxy resin manufactured by Yuka-Shell Epoxy Co., Ltd., epoxy equivalent: 182 to 194), 114.0 parts of bisphenol A and 29.2 parts of acetic acid were weighted in a reaction vessel equipped with a stirrer, a cooling tube, a nitrogen introducing tube and a thermometer. The reaction mixture was heated to 130° C. under nitrogen atmosphere. 0.15 Part of dimethylbenzylamine was added to the mixture. The exothermic reaction was maintained at 170° C. for 1 hour to give a bisphenol A type epoxy resin (epoxy equivalent: 649).

[0139] Subsequently, the reaction system was cooled to 140° C. 396.8 Parts of 2-ethylhexanol-halfblocked IPDI as prepared above were added to the reaction mixture. The reaction was maintained at 140° C. for 1 hour. Subsequently, 323.2 parts of ethylene glycol monobutyl ether were added to dilute the mixture. The reaction mixture was cooled to 100° C., and then 188.8 parts of 78.3% MI BK solution containing methyl isobutyl mono-ketiminated compound of aminoethyl ethanolamine were added.

[0140] The mixture was maintained at 110° C. for 1 hour, and then cooled to 90° C., thereto 360.0 parts of ion-exchange water were added. The reaction system was maintained with stirring for further 30 minutes to convert the
ketimine moieties in the epoxy resin to the corresponding primary amino groups. Excess amount of water and MIBK were removed from the mixture in vacuo. Dilution with 588.1 parts of ethylene glycol monobutyl ether gave a primary amino group-containing pigment dispersion resin (resin solid contents: 50%).

**Preparation Example B6**

**Preparation of Pigment Dispersed Paste**

<table>
<thead>
<tr>
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<td>20</td>
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<td>50</td>
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<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>(Pore volume: 0.8 ml/g, Average particle size: 2.5 μm)</td>
<td></td>
<td></td>
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<tr>
<td>Silica particles B</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
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<tr>
<td>(Pore volume: 1.6 ml/g, Average particle size: 4.0 μm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Silica particles C</td>
<td>0</td>
<td>0</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>(Pore volume: 0.44 ml/g, Average particle size: 6.5 μm)</td>
<td></td>
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<tr>
<td>Content of silica compound in pigments</td>
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<td>30</td>
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</table>

*Silica particles: SYL595 530 manufactured by FUJI SILYSIA CHEMICAL LTD.
*Silica particles: SYL595 350 manufactured by FUJI SILYSIA CHEMICAL LTD.
*Silica particles: SYL595 770 manufactured by FUJI SILYSIA CHEMICAL LTD.

**TABLE 3**

**Example B2**

An amine modified epoxy resin of Preparation Example B1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example B2 and the polyisocyanate curing agent of Preparation Example B3) were homogeneously mixed (resin : curing agent=60:40 as basis of solid contents). 90% Acetic acid was added to the mixture to achieve 38.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1100.0 Parts of the main emulsion, 400.0 parts of the resin emulsion of the Preparation Example B4 and 540.7 parts of pigment dispersed paste B3 were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide. Ethyleneglycol monohexyl ether was added to provide film resistance of 1200. Acetic acid was added to provide minimum deposition pH of 11.96. A cationic electrodeposition coating composition was prepared in solid contents of 20.0%.

Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 μm. The coated plate was baked at 170° C. for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Pipe-throwing power was also evaluated. Results are shown in Table 4.

**Example B3**

An amine modified epoxy resin of Preparation Example B1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example B2 and the polyisocyanate curing agent of Preparation Example B3) were homoge-
neously mixed (resin : curing agent=50:50 as basis of solid contents). 90% Acetic acid was added to the mixture to achieve 38.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1100.0 Parts of the main emulsion, 400 parts of the resin emulsion of the Preparation Example B4 and 541.7 parts of pigment dispersed paste BC were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide. Ethyleneglycol monohexyl ether was added to provide film resistance of 1400. Acetic acid was added to provide minimum deposition pH of 11.91. A cationic electrodeposition coating composition was prepared in solid contents of 20.0%.

[0147] Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 µm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Pipe-throwing power was also evaluated. Results are shown in Table 4.

Comparative Example B1

[0148] An amine modified epoxy resin of Preparation Example B1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example B2 and the polyisocyanate curing agent of Preparation Example B3 (weight ratio of the agents, Preparation Example B2/Preparation Example B3=1/1)) were homogeneously mixed (resin : curing agent=80:20 as basis of solid contents). 90% Acetic acid was added to the mixture to achieve 38.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1100.0 Parts of the main emulsion, 400 parts of the resin emulsion of the Preparation Example B4 and 541.7 parts of pigment dispersed paste BF were mixed with 1949.3 parts of ion-exchange water and 9.0 parts of dibutyltin oxide. Ethylene glycol monohexyl ether was added to provide film resistance of 1200. Acetic acid was added to provide minimum deposition pH of 11.95. A cationic electrodeposition coating composition was prepared in solid contents of 20.0%.

[0149] Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 µm. The coated plate was baked at 170°C for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Pipe-throwing power was also evaluated. Results are shown in Table 4.

Comparative Example B2

[0150] An amine modified epoxy resin of Preparation Example B1 and a blocked polyisocyanate curing agent (a mixture of the polyisocyanate curing agent of Preparation Example B2 and the polyisocyanate curing agent of Preparation Example B3 (weight ratio of the agents, Preparation Example B2/Preparation Example B3=9/1)) were homogeneously mixed (resin : curing agent=95.5 as basis of solid contents). 90% Acetic acid was added to the mixture to achieve 38.0% of neutralization ratio and ion-exchange water was added to dilute gradually. MIBK was removed in vacuo to give a main emulsion (36.0% solid contents). 1100.0 Parts of the main emulsion, 400 parts of the resin emulsion of the Preparation Example B4 and 541.7 parts of pigment dispersed paste BF were mixed with 1949.3 parts...
of ion-exchange water and 9.0 parts of dibutyltin oxide. Ethyleneglycol monohexyl ether was added to provide film resistance of 1200. Acetic acid was added to provide minimum deposition pH of 11.96. A cationic electrodeposition coating composition was prepared in solid contents of 20.0%.

[0155] Thus prepared cationic electrodeposition coating composition was electrodeposited on a zinc coated steel plate so that thickness of the resulting cured coating film was 7 μm. The coated plate was baked at 170° C. for 30 minutes in an oven to give an electrodeposited coating film. Corrosion resistance of the film was evaluated. Pipe-throwing power was also evaluated. Results are shown in Table 4.

[0156] The electrodeposited coating films and cured coating films thereof which were prepared with the cationic electrodeposition coating compositions which had been obtained in the Examples and Comparative Examples were each evaluated by the following methods.

<Pipe-throwing Power>

[0157] Throwing power of the individual cationic electrodeposition coating composition, which had been prepared in each Examples and Comparative Examples, was measured in an apparatus illustrated in FIG. 3. 3 L of electrodeposition coating composition (207) which had been previously prepared was poured into a conductive electrodeposition coating vessel (201) (inner diameter: 105 mm, height: 370 mm) with stirrer (205) and stirred. A specimen plate (203) (size: 15 mm×400 mm, thickness: 0.7 mm) of a steel plate which had been treated with zinc phosphate (wherein SURFDINE SD-2500 treatment defined in JIS G 3141 SPCC-SD was employed) was used. A pipe having open-ends (202) (inner diameter: 17.5 mm, longitudinal length 375 mm, wall thickness: 1.8 mm) was to be telescopically set into the coating vessel (201). The specimen plate (203) was placed in the pipe (202) without contacting each other. Both specimen plate (203) and pipe (202) were immersed together in the electrodeposition coating composition. Each longitudinal length of the immersed parts of specimen plate (203) and pipe (202) was 30 cm.

[0158] Electrodeposition coating was conducted by applying voltage between coating vessel (201) as an anode and specimen plate (203) as a cathode. Voltage was gained to 240 V in 30 seconds immediately after its application and maintained at a given value for 150 seconds during the coating. Temperature inside of the vessel was adjusted at 28° C. Coated specimen plate was washed with water, and then baked at 150° C. for 25 minutes. Longitudinal length of the coated part on the specimen plate, i.e., distance from the bottom line of the specimen plate (which is aligned with the immersed end of the pipe) to the uncoated part, was measured. Pipe-throwing power is represented by ratio of the coated length to the immersed length (cm/cm) in the following Table 4.

<Film Resistance of Electrodeposited Coating Film>

[0159] A steel plate, which had been treated with zinc phosphate (wherein SURFDINE SD-2500 treatment defined in JIS G 3141 SPCC-SD was employed) (size: 70 mm×150 mm, thickness: 0.7 mm), was immersed into a cationic electrodeposition coating composition in an electrodeposition bath (length of the immersed part was 10 cm). Voltage was applied to the steel plate and gained to 240 V over 30 seconds, and maintained for 150 seconds during the electrodeposition coating. Measuring the residual current and thickness of the resulted coating film after baking, value of film resistance (kΩ·cm²) was calculated on the assumption that thickness of the electrodeposited coating film would be 15 μm.

<Minimum Deposition pH>

[0160] A steel plate which had been treated with zinc phosphate (wherein SURFDINE SD-2500 treatment defined in JIS G 3141 SPCC-SD was employed) was masked so that the coating area was to be 50 mm×50 mm. The masked plate was immersed into one of the cationic electrodeposition coating compositions (4 L) which had been prepared in the Examples and Comparative Examples in an electrodeposition coating bath. Constant-current electrodeposition coating was conducted by applying voltage at current density of 1 mA/cm² at 28° C. Minimum deposition pH was determined according to the method as described above.

<Corrosion Resistance>

[0161] Corrosion resistance was evaluated by cyclemode disclosed in JP-A-2000-113726. Evaluation basis is as follows.

[0162] ☐ : No more than 30% of blister occurring area after 120 cycles

[0163] ○ : No more than 50% of blister occurring area after 120 cycles

[0164] X : No more than 80% of blister occurring area after 120 cycles

[0165] XX : No less than 80% of blister occurring area after 120 cycles

### TABLE 4

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Pore volume</td>
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<td>1.6 ml/g</td>
<td>0.44 ml/g</td>
<td>0.8 ml/g</td>
<td>—</td>
<td>—</td>
<td>1.6 ml/g</td>
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<tr>
<td>Average particle size</td>
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<td>4 μm</td>
<td>6.5 μm</td>
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<td>—</td>
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<td>4 μm</td>
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<tr>
<td>Minimum deposition pH</td>
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<td>11.94</td>
<td>12.05</td>
<td>11.95</td>
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<td>1100</td>
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<td>Film resistance (Thickness: 15 lm, Voltage: 240 V)</td>
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<td>80/20</td>
<td>50/50</td>
<td>80/20</td>
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</tr>
<tr>
<td>Pipe-three power</td>
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<tr>
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</tr>
</tbody>
</table>

The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising”, “having”, “including”, and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those skilled in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.


1. A cationic electrodeposition coating composition comprising silica particles having pore volume of 0.44 to 1.8 ml/g and average particle size of no more than 10 μm, the composition showing square root of diffusion coefficient (ν/χc) of no less than 2.5 upon diffusing a solution onto a coating film therewith.

2. The cationic electrodeposition coating composition according to claim 1, which further comprises an amine modified epoxy resin (A) and a blocked isocyanate curing agent (B), wherein weight ratio of the amine modified epoxy resin (A) to the blocked isocyanate curing agent (B) is 50:50 to 90:10 (A/B), and the blocked isocyanate curing agent (B) comprises a blocked aliphatic polyisocyanate and a blocked aromatic polyisocyanate, wherein weight ratio of the blocked aliphatic polyisocyanate to the blocked aromatic polyisocyanate is 3/1 to 1/3 (the blocked aliphatic polyisocyanate/the blocked aromatic polyisocyanate).

3. The cationic electrodeposition coating composition according to claim 1, wherein content of the silica particles is 1 to 30% by weight relative to total weight of pigments.

4. An article coated with the cationic electrodeposition coating composition according to claim 1.

5. A cationic electrodeposition coating composition comprising silica particles having pore volume of 0.44 to 1.8 ml/g and average particle size of no more than 10 μm, wherein the composition shows minimum deposition pH of 11.90 to 12.00 during electrodeposition coating, and film resistance of 1,000 to 1,500 kΩ·cm² at film thickness of 15 μm and applied voltage of 240 V.

6. The cationic electrodeposition coating composition according to claim 5, which further comprises an amine modified epoxy resin (A) and a blocked isocyanate curing agent (B), wherein weight ratio of the amine modified epoxy resin (A) to the blocked isocyanate curing agent (B) is 50/50 to 90/10 (A/B), and the blocked isocyanate curing agent (B) comprises a blocked aliphatic polyisocyanate and a blocked aromatic polyisocyanate, wherein weight ratio of the blocked aliphatic polyisocyanate to the blocked aromatic polyisocyanate is 3/1 to 1/3 (the blocked aliphatic polyisocyanate/the blocked aromatic polyisocyanate).

7. The cationic electrodeposition coating composition according to claim 5, wherein content of the silica particles is 1 to 30% by weight relative to total weight of pigments.
8. An article coated with the cationic electrodeposition coating composition according to claim 5.
9. An article coated with the cationic electrodeposition coating composition according to claim 2.
10. An article coated with the cationic electrodeposition coating composition according to claim 3.

11. An article coated with the cationic electrodeposition coating composition according to claim 6.
12. An article coated with the cationic electrodeposition coating composition according to claim 7.

* * * * *