



US 20050161330A1

(19) **United States**(12) **Patent Application Publication****Toi et al.**(10) **Pub. No.: US 2005/0161330 A1**(43) **Pub. Date: Jul. 28, 2005**(54) **PROCESS FOR FORMING MULTI LAYERED COATED FILM AND MULTI LAYERED COATED FILM**(52) **U.S. Cl. 204/484; 204/487**(76) **Inventors: Teruzo Toi, Osaka-shi (JP); Yasuo Mihara, Souraku-gun (JP)**(57) **ABSTRACT**

Correspondence Address:
WENDEROTH, LIND & PONACK, L.L.P.
2033 K STREET N. W.
SUITE 800
WASHINGTON, DC 20006-1021 (US)

The present invention provides a process for forming a multi layered coated film having good finished appearance. The present invention relates to a process for forming a multi layered coated film comprising the steps of conducting electrodeposition coating with a cationic electrodeposition coating composition on a substrate, and then heating and curing it to form an cured electrodeposition coated film on the substrate, applying an intermediate coating composition on the cured coated film to form an uncured intermediate coated film, applying a base top coating composition on the uncured intermediate coated film to form an uncured base coated film, applying a clear top coating composition on the uncured base coated film to form an uncured clear coated film, and simultaneously heating and curing the three uncured coated films, wherein the cured electrodeposition coated film has specified ranges of Ra and Pa; or has specified ranges of Tg and crosslinking density.

(21) **Appl. No.: 11/042,067**(22) **Filed: Jan. 26, 2005**(30) **Foreign Application Priority Data**

Jan. 26, 2004 (JP) 2004-17107
 Jan. 26, 2004 (JP) 2004-17109

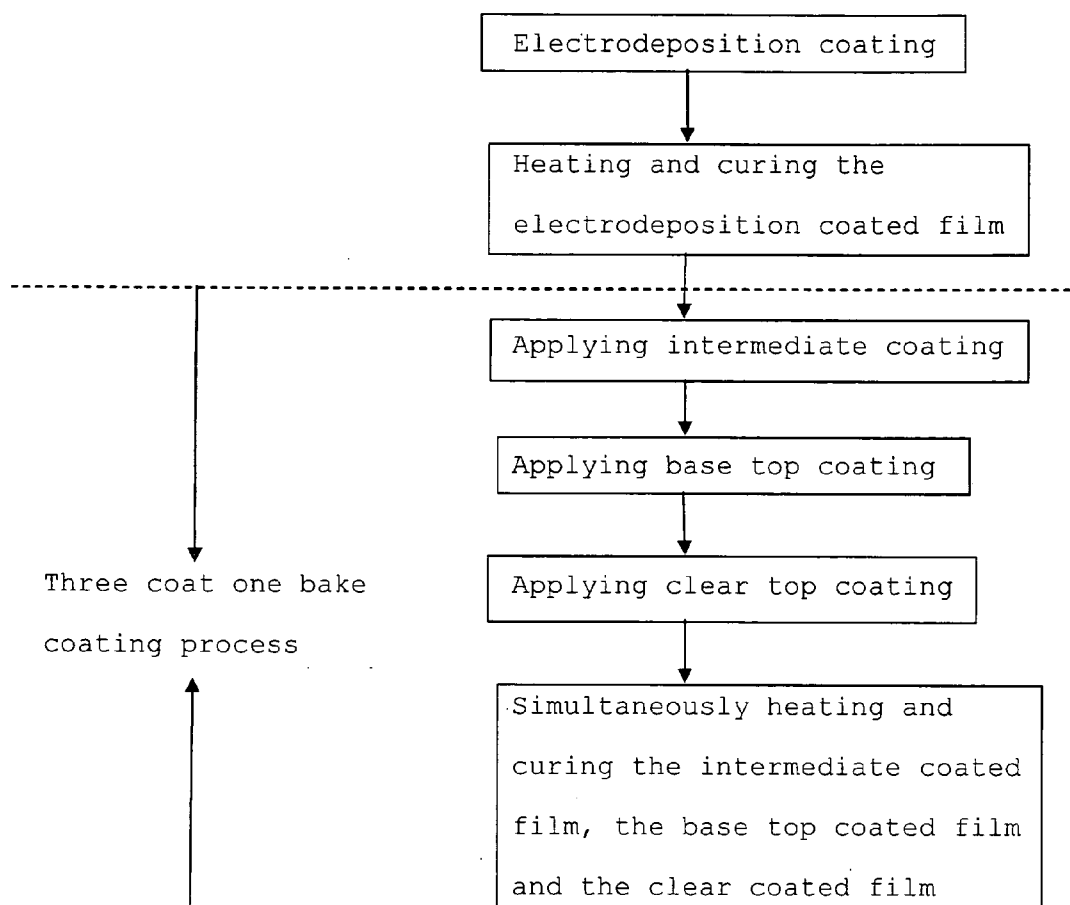
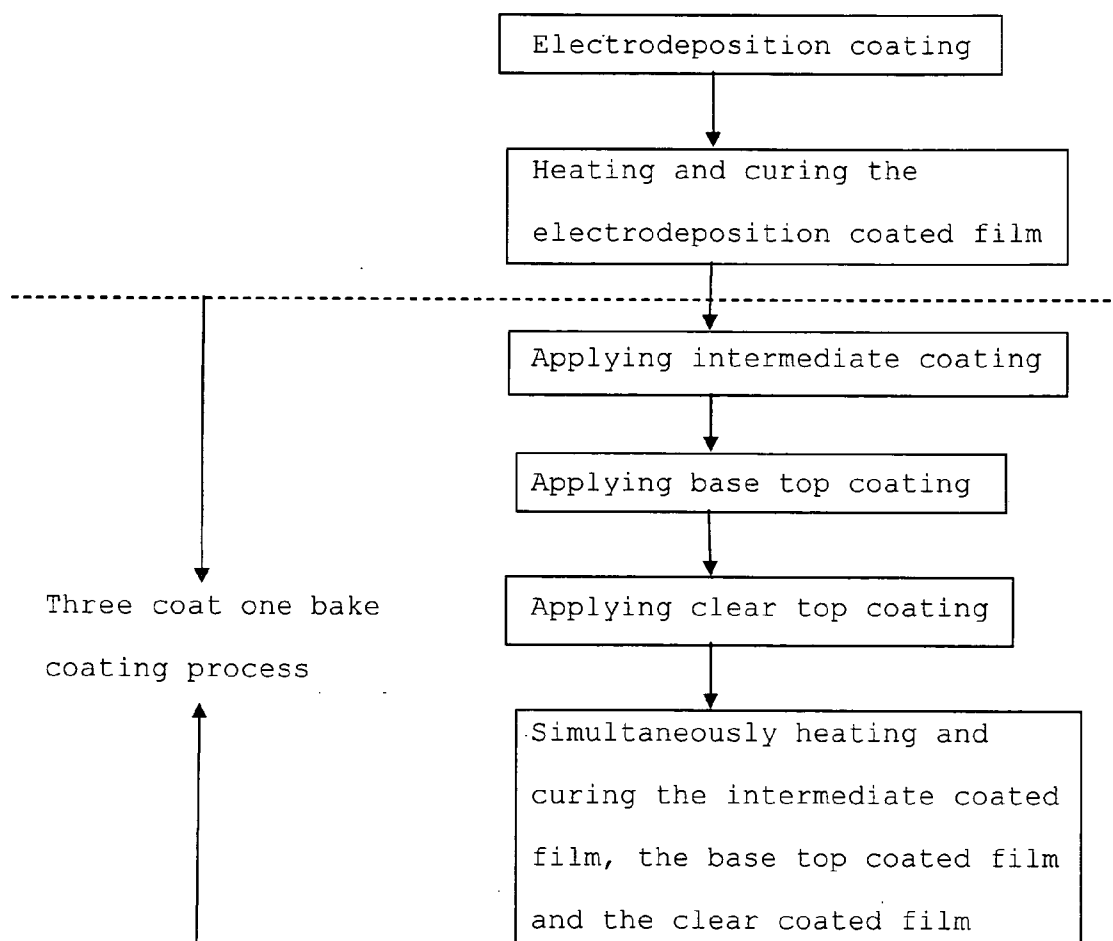
Publication Classification(51) **Int. Cl.⁷ C23C 28/00**

Fig.1



PROCESS FOR FORMING MULTI LAYERED COATED FILM AND MULTI LAYERED COATED FILM

FIELD OF THE INVENTION

[0001] The present invention relates to a process for forming a multi layered coated film having good finished appearance.

BACKGROUND OF THE INVENTION

[0002] Multi layers of coated films having various functions are formed on the surface of a substrate of automobile body to protect the substrate and impart the substrate into good appearance. However, in recent years, a process for forming a multi layered coated film comprising the steps of: applying the next coated film on an uncured coated film by so-called wet on wet coating; and simultaneously baking the multi layers; without the step of baking the uncured coated film after applying every layer has been used because of a requirement of saving energy and reducing cost.

[0003] As an example of the process, a three coat one bake coating process (three wet coating) comprising the steps of: applying an intermediate coating, a base top coating and a clear top coating on an cured electrodeposition coated film by wet on wet coating; and simultaneously baking and curing the three layers of uncured coated films; is considered to be the most practical process. A schematic flow chart of the coating process is shown in **FIG. 1**.

[0004] In Japanese Patent Kokai Publication No. 277474/1998, a process for forming a multi layered coated film comprising the steps of: applying an intermediate coating, a metallic coating and a clear top coating on a substrate to be coated in the order; and simultaneously baking the three layers of the coated films; is disclosed. It is described therein that the process provides the coated film having excellent vividness and excellent lustrousness.

[0005] In the three coat one bake coating process shown in **FIG. 1**, it has been found that the surface condition of the cured electrodeposition coated film has a great effect on an appearance of the multi layered coated film. The reason is considered that the three coat one bake coating process has smaller number of baking step as described above. In the above process for forming a multi layered coated film (Japanese Patent Kokai Publication No. 277474/1998), the surface condition of the electrodeposition coated film for improving the appearance of the multi layered coated film is not described.

[0006] In Japanese Patent Kokai Publication No. 224613/2002, a process for forming a multi layered coated film comprising the steps of: forming a cured electrodeposition coated film on a substrate from a cationic electrodeposition coating composition; applying three layers of coatings on the cured electrodeposition coated film by a three coat one bake coating process; and simultaneously baking and curing the three layers of uncured coated films; wherein the cured electrodeposition coated film has a glass transition temperature of not less than 110° C. and a surface roughness (Ra: centerline average roughness) of not more than 0.3 μm ; is disclosed. In this process, only the centerline average roughness (Ra) is used as a parameter for evaluating the appearance of the coated film, but the other parameters are not used.

[0007] Moreover, in the three coat one bake coating process shown in **FIG. 1**, a composition for the intermediate coating are applied on the cured electrodeposition coated film. There is a case that a solvent contained in the composition for the intermediate coating is absorbed in the cured electrodeposition coated film during applying the composition. The solvent absorbed in the cured electrodeposition coated film is volatilized during baking the laminated coated film to affect the intermediate coated film and the like, which degrades the finished appearance of the laminated coated film. It has been found that the solvent contained in the uncured intermediate coated film applied on the cured electrodeposition coated film has a great effect on the cured electrodeposition coated film, because the number of baking step is small and the uncured coated films laminated to two or more layer are simultaneously baked in the three coat one bake coating process. In the above process for forming a multi layered coated film (Japanese Patent Kokai Publication No. 277474/1998), physical properties of the electrodeposition coated film are not described for improving the appearance of the multi layered coated film.

OBJECTS OF THE INVENTION

[0008] A main object of the present invention is to provide a process for forming a multi layered coated film having good finished appearance in a three coat one bake coating process which can save energy and reduce cost.

[0009] In the present invention, a process for obtaining a coated film having good finished appearance has been found. In according to the process of the present invention, a multi layered coated film having good appearance can be obtained even in the three coat one bake coating process having smaller number of baking step. The multi layered coated film contains an electrodeposition coated film, an intermediate coated film, a base top coated film and a clear top coated film. In according to the process of the present invention, energy required for baking and curing in the coating step can be saved, and production cost can be reduced. The process of the present invention can be suitably used in the art that energy saving during the application and good appearance are required.

[0010] This object as well as other objects and advantages of the present invention will become apparent to those skilled in the art from the following description with reference to the accompanying drawing.

BRIEF EXPLANATION OF DRAWINGS

[0011] The present invention will become more fully understood from the detailed description given hereinafter and the accompanying drawing which is given by way of illustration only, and thus are not limitative of the present invention, and wherein:

[0012] **FIG. 1** is a flow chart illustrating one embodiment of the process of the present invention.

SUMMARY OF THE INVENTION

[0013] The present invention provides a process for forming a multi layered coated film comprising the steps of:

[0014] conducting electrodeposition coating with a cationic electrodeposition coating composition on a substrate, and then heating and curing it to form an

cured electrodeposition coated film on the substrate, applying an intermediate coating composition on the cured electrodeposition coated film to form an uncured intermediate coated film,

[0015] applying a base top coating composition on the uncured intermediate coated film to form an uncured base coated film

[0016] applying a clear top coating composition on the uncured base coated film to form an uncured clear coated film, and

[0017] simultaneously heating and curing the uncured intermediate coated film, the uncured base top coated film and the uncured clear coated film; wherein

[0018] the cured electrodeposition coated film has a centerline average roughness (Ra) of 0.05 to 0.25 μm obtained from a roughness curve and a centerline average roughness (Pa) of 0.05 to 0.30 μm obtained from a profile curve, thereby accomplishing the object described above.

[0019] The present invention also provides a process for forming a multi layered coated film comprising the steps, wherein the cured electrodeposition coated film has a surface energy of 37 to 43 mJ/m^2 , and the intermediate coating composition has a contact angle of 10 to 30 degrees on the cured electrodeposition coated film, thereby accomplishing the object described above.

[0020] The present invention also provides a process for forming a multi layered coated film comprising the steps, wherein the cured electrodeposition coated film has a centerline average roughness (Ra) of 0.05 to 0.25 μm obtained from a roughness curve, a centerline average roughness (Pa) of 0.05 to 0.30 μm obtained from a profile curve and a surface energy of 37 to 43 mJ/m^2 , and the intermediate coating composition has a contact angle of 10 to 30 degrees on the cured electrodeposition coated film, thereby accomplishing the object described above.

[0021] The present invention also provides a process for forming a multi layered coated film comprising the steps, wherein the cured electrodeposition coated film has a glass transition temperature Tg of 100 to 130° C. and a crosslinking density of 1.2 to 2.6 mmol/cc, obtained by dynamic viscoelastic measurement, thereby accomplishing the object described above.

[0022] The process to accomplish the present invention will be explained in detail. The present inventors have suggested a method of evaluating the cured electrodeposition coated film by the surface roughness (Ra: centerline average roughness) in Japanese Patent Kokai Publication No. 224613/2002.

[0023] It is difficult to evaluate the appearance of the coated film by a single method, because surface morphology, optical properties and color complexly visually affect the appearance. In an evaluation of the appearance by wavelength as a method of evaluating the appearance of the coated film, for example, roughness related to gloss and vividness can be evaluated by short wavelength and roughness related to winding can be evaluated by long wavelength. In JIS related to the surface roughness, it is described

that a contour curve can be divided into a profile curve (P), roughness curve (R) and winding curve (W).

[0024] The appearance of the coated film can be evaluated by classifying it into items of smoothness, orange peel and luster. In the present invention, it has been found for the Ra value (centerline average roughness in the roughness curve) of the cured electrodeposition coated film used in the conventional evaluating method to have a correlation to the item of orange peel. It has been found for the Wa value (centerline average roughness in the winding curve) of the cured electrodeposition coated film as a parameter related to the winding curve (W) to have a correlation to the item of smoothness in the appearance of the multi layered coated film. In addition, it has been found for the winding measured by long wavelength to have great effect on the appearance of the resulting multi layered coated film. Moreover, it has been found to improve the finished appearance of the resulting multi layered coated film by evaluating the cured electrodeposition coated film using the Ra value and the Pa value (centerline average roughness in the profile curve) containing both the Ra value and Wa value as parameters to control the surface condition, thereby accomplishing one embodiment of the present invention.

[0025] It is considered that the multi layered coated film having good appearance is not occasionally obtained when the intermediate coating composition has low wettability with the cured electrodeposition coated film, even if controlling the surface condition of the cured electrodeposition coated film as described above during the formation of the multi layered coated film in the three coat one bake coating process as described in the present invention. Such defect has great effect on the appearance of the resulting multi layered coated film, because the three coat one bake coating process has smaller number of baking step.

[0026] In the present invention, it has been found that the wettability of the intermediate coated film can be controlled by adjusting the surface energy of the cured electrodeposition coated film to a specified range, and the finished appearance of the resulting multi layered coated film can be improved, thereby accomplishing another embodiment of the present invention.

[0027] In the present invention, it has been found that the solvent resistance of the cured electrodeposition coated film can be improved by adjusting the glass transition temperature Tg and crosslinking density from dynamic viscoelastic measurement of the cured electrodeposition coated film to specified ranges, and the finished appearance of the resulting multi layered coated film can be improved, thereby accomplishing further another embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0028] In one embodiment of the present invention, components contained in a cationic electrodeposition coating composition and the content thereof are selected such that the cured electrodeposition coated film formed by electrodeposition coating has a centerline average roughness (Ra) of 0.05 to 0.25 μm obtained from a roughness curve and a centerline average roughness (Pa) of 0.05 to 0.30 μm obtained from a profile curve. The upper limit of the centerline average roughness (Ra) is preferably 0.20 μm .

The upper limit of the centerline average roughness (Pa) is preferably 0.25 μm . It is difficult to obtain the cured electrodeposition coated film having a centerline average roughness (Ra) and centerline average roughness (Pa) of smaller than the lower limit of 0.05 μm in the level of the current technology.

[0029] The centerline average roughness (Ra) obtained from a roughness curve and the centerline average roughness (Pa) obtained from a profile curve as used herein are parameters defined in JIS B 0601. The centerline average roughness (Ra) obtained from the roughness curve and the centerline average roughness (Pa) obtained from the profile curve of the cured electrodeposition coated film can be measured, for example, by using an evaluation type surface roughness tester manufactured by Mitutoyo Corporation according to JIS B 0601.

[0030] When the Ra value is larger than 0.25 μm , the appearance of the multi layered coated film, particularly orange peel, is degraded. When the Pa value is larger than 0.30 μm , the appearance of the multi layered coated film, particularly smoothness, is degraded.

[0031] A method of preparing the cationic electrodeposition coating composition for obtaining the cured electrodeposition coated film having the centerline average roughness (Ra) obtained from the roughness curve and the centerline average roughness (Pa) obtained from the profile curve within the above ranges, includes a method of adjusting the type and content of the cationic epoxy resin, blocked isocyanate curing agent and catalyst in the cationic electrodeposition coating composition. Particularly, the type and content of the blocked isocyanate curing agent has a great effect on the Ra and Pa values. The flowability and curing rate of the coated film during forming the film (deposited film) are improved to improve the smoothness of the coated film by adjusting the solid content ratio between the cationic epoxy resin and blocked isocyanate curing agent. The smoothness of the electrodeposition coated film can be further improved by using the surface treated steel plate having smaller surface roughness.

[0032] In another embodiment of the present invention, the cationic electrodeposition coating composition and intermediate coating composition are used such that the cured electrodeposition coated film formed has a surface energy of 37 to 43 mJ/m^2 , and the intermediate coating composition coated has a contact angle of 10 to 30 degrees on the cured electrodeposition coated film. When the surface energy of the cured electrodeposition coated film is within the above range and the contact angle between the cured electrodeposition coated film and intermediate coating composition is within the range of 10 to 30 degrees, the wettability of the intermediate coating composition to the cured electrodeposition coated film is high, and the finished appearance of the resulting multi layered coated film.

[0033] The surface energy of the cured electrodeposition coated film has the lower limit of preferably 38 mJ/m^2 , more preferably 39 mJ/m^2 , and has the upper limit of preferably 42 mJ/m^2 , more preferably 41 mJ/m^2 . The contact angle between the cured electrodeposition coated film and intermediate coating composition has the lower limit of preferably 10 degrees and has the upper limit of preferably 25 degrees.

[0034] When the surface energy is lower than 37 mJ/m^2 , the adhesion between the cured electrodeposition coated

film and intermediate coated film is degraded. On the other hand, when the surface energy is higher than 43 mJ/m^2 , the wettability of the intermediate coating composition to the cured electrodeposition coated film is degraded. In addition, when the contact angle between the cured electrodeposition coated film and intermediate coating composition is larger than 30 degrees, the wettability of the intermediate coating composition to the cured electrodeposition coated film is degraded.

[0035] The surface energy of the coated film is force applied in the perpendicular direction to free length. The surface energy is determined by measuring a contact angle between the coated film and three kinds of liquids (such as water, methylene iodide and ethylene glycol) having known γ^{LW} value based on the Lifshitz-van der Waals forces, an acidic component γ^+ based on acid-base force and an basic component γ^- based on acid-base force in a contact angle process; obtaining γ^{LW} , γ^+ and γ^- values of the coated film from the following equation 1 led from Young-Dupre Equation; and calculating from the values using the following equation 2 (See C. J. Van Oss, "J. Protein Chem", Vol. 4, 245, 1985 and C. J. Van Oss, "J. Colloid Interface Sci", Vol. 111, 378, 1986).

$$2\{(\gamma_i^{\text{LW}} \cdot \gamma_j^{\text{LW}})^{1/2} + (\gamma_i^+ \cdot \gamma_j^-)^{1/2} + (\gamma_i^- \cdot \gamma_j^+)^{1/2}\} = \quad \text{Equation 1}$$

$$(1 + \cos\theta)\{\gamma_i^{\text{LW}} + 2(\gamma_i^+ \cdot \gamma_j^-)^{1/2}\}$$

$$\text{Surface free energy}(\gamma) = \gamma_i^{\text{LW}} + (\gamma_j^+ \cdot \gamma_j^-)^{1/2} \quad \text{Equation 2}$$

[0036] γ_i^{LW} a term based on the Lifshitz-van der Waals forces of the liquid

[0037] γ_i^+ : an acidic component based on acid-base force of the liquid

[0038] γ_i^- : an basic component based on acid-base force of the liquid

[0039] Θ : contact angle

[0040] A method of preparing the cationic electrodeposition coating composition and intermediate coating composition, from which the surface energy of the cured electrodeposition coated film and the contact angle between the cured electrodeposition coated film and the intermediate coating composition within the above ranges can be obtained, includes a method of adjusting the type and the content of the cationic epoxy resin, blocked isocyanate curing agent, catalyst and surface conditioner contained in the cationic electrodeposition coating composition. Particularly, the type and the content of the surface conditioner have a great effect on the surface energy and the contact angle between the cured electrodeposition coated film and the intermediate coating composition. The types of the surface conditioner used in the present invention include acryl-based type, silicone-based type and vinyl-based type.

[0041] In the process for forming a multi layered coated film of the present invention, it is more preferable that the cured electrodeposition coated film have a centerline average roughness (Ra) of 0.05 to 0.25 μm obtained from a roughness curve and a centerline average roughness (Pa) of 0.05 to 0.30 μm obtained from a profile curve and the contact angle between the cured electrodeposition coated film and

intermediate coating composition is within the range of 10 to 30 degrees. This is because the multi layered coated film having more excellent finished appearance can be obtained.

[0042] In the present invention, components contained in a cationic electrodeposition coating composition and the content thereof are selected such that the cured electrodeposition coated film formed by electrodeposition coating has a specified range of glass transition temperature Tg (which is also represented by "dynamic Tg" herein) and a specified range of crosslinking density, obtained by dynamic viscoelastic measurement.

[0043] The dynamic Tg as used herein is determined by measuring a dynamic glass transition temperature Tg using a sample in the same way as a general measuring method of Tg by dynamic viscoelastic measurement. Examples of the measuring methods used in the present invention include a method of performing dynamic viscoelastic measurement using the sample prepared by forming a cured electrodeposition coated film on a substrate, separating the coated film using mercury and cutting it. In the method, the sample was heated from room temperature to 200° C. at a raising rate of temperature of 2° C. per one minute and vibrated at a frequency of 11 Hz to determine viscoelasticity thereof. A ratio ($\tan \delta$) of storage elasticity (E')/loss elasticity (E'') was calculated and its inflexion point (a temperature at a peak of $\tan \delta$) was determined to obtain a dynamic Tg. Example of a measuring apparatus of dynamic viscoelastic includes, for example, Rheovibron model RHEO 2000, 3000 (trade name), manufactured by Orientec Co., Ltd.

[0044] In the present invention, it is preferable for the cured electrodeposition coated film formed by electrodeposition coating to have a dynamic Tg of 100 to 130° C. The lower limit of the dynamic Tg is preferably 110° C. and the upper limit of the dynamic Tg is preferably 125° C. When the dynamic Tg of the cured electrodeposition coated film is lower than 100° C., the electrodeposition coated film swells with a solvent contained in the intermediate coating composition, and the finished appearance of the resulting multi layered coated film is degraded. On the other hand, when the dynamic Tg is higher than 130° C., the elastic modulus of the resulting multi layered coated film is low, and the impact resistance the coated film is degraded.

[0045] The crosslinking density is determined by measuring dynamic viscoelasticity of the cured electrodeposition coated film formed by electrodeposition coating in the same way as the measuring method of the dynamic Tg, and calculating with the resulting storage elasticity (E') in rubbery region from the following equation:

$$E' = 3nRT$$

[0046] wherein E' is storage elasticity; n is crosslinking density; R is gas constant; and T is absolute temperature.

[0047] In the present invention, the crosslinking density of the cured electrodeposition coated film formed by electrodeposition coating is within the range of preferably 1.2 to 2.6 mmol/cc. The lower limit of the crosslinking density is more preferably 1.4 mmol/cc and the upper limit is more preferably 2.3 mmol/cc. When the crosslinking density of the cured electrodeposition coated film is lower than 1.2 mmol/cc, the electrodeposition coated film swells with a solvent contained in the intermediate coating composition, and the finished appearance of the resulting multi layered

coated film is degraded. On the other hand, when the crosslinking density is higher than 2.6 mmol/cc, blisters easily occur by containing water, and the corrosion resistance is degraded.

[0048] A method of preparing the cationic electrodeposition coating composition for obtaining the cured electrodeposition coated film having the dynamic Tg and the crosslinking density within the above ranges includes a method of adjusting the type and content of the cationic epoxy resin, blocked isocyanate curing agent and catalyst in the cationic electrodeposition coating composition. Particularly, the type and content of the cationic epoxy resin and the blocked isocyanate curing agent have a great effect on the dynamic Tg and crosslinking density. Examples of the cationic epoxy resins include resins obtained by opening the epoxy ring of bisphenol A type epoxy resin or bisphenol F type epoxy resin with activated hydrogen compound, into which a cationic group can be introduced. Examples of the blocked isocyanate curing agents include hexamethylene diisocyanate (comprising trimer), tetramethylene diisocyanate and trimethylhexamethylene diisocyanate; cycloaliphatic diisocyanates, such as and 4,4'-methylene bis(cyclohexylisocyanate); aromatic diisocyanates such as tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) blocked with a suitable block agent. In addition, the dynamic Tg and crosslinking density can be also adjusted by selecting the ratio of the blocked isocyanate curing agent to the cationic epoxy resin or the baking temperature of the electrodeposition coated film.

[0049] The materials to be coated, cationic electrodeposition coating composition, intermediate coating composition, base top coating composition and clear top coating composition used in the process for forming a multi layered coated film of the present invention, and applying methods thereof will be explained hereinafter.

[0050] Substrates to be Coated

[0051] The substrates to be coated used in the process for forming a multi layered coated film of the present invention may be any substrates, which can be electrodeposition coated. Examples of the substrates include metals such as iron, steel, aluminum, tin, zinc and the like, and alloys thereof, and plated articles thereof or deposited articles thereof. The concrete examples thereof include passenger car, motor truck, motorcycle, bus and the like, manufactured by using the metallic components. Moreover, plastic materials obtained by conductive treating resins such as polyethylene resin, polypropylene resin, ethylene-vinyl acetate copolymer resin, polyamide resin, acrylic resin, vinylidene chloride, polycarbonate resin, polyurethane resin, epoxy resin, and various FRP, may be used as the substrate.

[0052] In the process for forming a multi layered coated film of the present invention, the substrate may be used as-received condition or after pre-treatment such as degreasing treatment or chemical conversion treatment prior to electrodeposition coating.

[0053] Cationic Electrodeposition Coating Composition

[0054] The cationic electrodeposition coating composition used in the present invention comprises binder resin containing aqueous solvent, cationic epoxy resin and blocked isocyanate curing agent dispersed or dissolved in the aque-

ous solvent; acid for neutralization; and organic solvent. The cationic electrodeposition coating composition may further contain pigment.

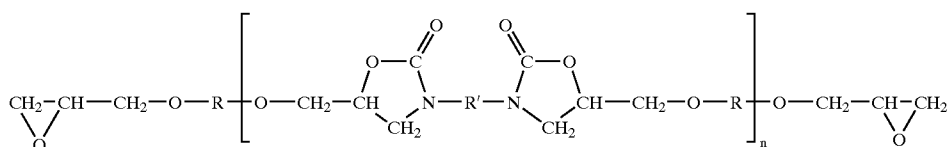
[0055] Cationic Epoxy Resin

[0056] The cationic epoxy resins used in the present invention include amine-modified epoxy resins. The cationic epoxy resins may be well known resins described in Japanese Patent Kokai Publication Nos. 4978/1979, 34186/1981 and the like.

[0057] The cationic epoxy resins are typically made by opening the all epoxy rings of bisphenol type epoxy resin with activated hydrogen compound, into which a cationic group can be introduced; or by opening a part of the epoxy rings with the other activated hydrogen compound and opening the residual epoxy rings with activated hydrogen compound, into which a cationic group can be introduced.

[0058] The concrete examples of the bisphenol type epoxy resins include bisphenol A type epoxy resins and bisphenol F type epoxy resins. Examples of the bisphenol A type epoxy resins, which are commercially available from Yuka Shell Epoxy Co., Ltd., include Epikote 828 (epoxy equivalent value: 180 to 190), Epikote 1001 (epoxy equivalent value: 450 to 500), Epikote 1010 (epoxy equivalent value: 3000 to 4000) and the like. Examples of the bisphenol F type epoxy resins, which are commercially available from Yuka Shell Epoxy Co., Ltd., include Epikote 807 (epoxy equivalent value: 170) and the like.

[0059] Oxazolidone ring containing epoxy resins having the following formula:



formula 1

[0060] wherein R represents a residual group obtained by removing glycidyl group from diglycidyl epoxy compound, R' represents a residual group obtained by removing isocyanate group from diisocyanate compound and n represents a positive integer,

[0061] may be used in the cationic epoxy resin because of obtaining a coated film having excellent heat resistance and corrosion resistance. This is because the coated film having excellent solvent resistance (solvent swelling resistance) can be obtained.

[0062] A method of introducing the oxazolidone ring into the epoxy resin includes a method comprising the steps of heating the blocked isocyanate curing agent blocked with lower alcohol such as methanol and polyepoxide under basic catalyst and keeping the temperature constant, and distilling the lower alcohol as a by-product off the system.

[0063] The particularly preferred epoxy resin is oxazolidone ring containing resin. This is because the coated film, which is superior in solvent resistance (solvent swelling resistance), heat resistance, corrosion resistance and impact resistance, can be obtained.

[0064] It is well known to obtain epoxy resins containing oxazolidone ring by reaction of bifunctional epoxy resin with diisocyanate blocked with monoalcohol (that is, bisurethane). The concrete examples of the oxazolidone ring containing epoxy resins and the preparing method thereof are disclosed in paragraphs [0012] to [0047] of Japanese Patent Kokai Publication No. 128959/2000, which are well known.

[0065] The epoxy resin may be modified with suitable resins, such as polyesterpolyol, polyetherpolyol, and monofunctional alkylphenol. In addition, the epoxy resins can be chain-extended by the reaction of epoxy group with diol or dicarboxylic acid.

[0066] It is desired for the epoxy resins to be ring-opened with activated hydrogen compound such that they have an amine equivalent value of 0.3 to 4.0 meq/g after ring opening, and particularly 5 to 50% thereof is primary amine group.

[0067] Examples of the activated hydrogen compounds, into which a cationic group can be introduced, include primary amine, secondary amine, and an acid salt of tertiary amine, sulfide and acid mixture. In order to prepare primary amine, secondary amine and/or tertiary amine containing epoxy resin, primary amine, secondary amine, and an acid salt of tertiary amine are used as the activated hydrogen compound, into which a cationic group can be introduced.

[0068] The concrete examples thereof include butylamine, octylamine, diethylamine, dibutylamine, methylbutylamine, an acid salt of triethylamine, an acid salt of N,N-dimethyl-

ethanolamine, diethyldisulfide-acetic acid mixture, and secondary amines obtained by blocking primary amines, such as ketimine of aminoethylethanolamine, ketimine of diethylenetriamine. The amines may be used in combination.

[0069] Blocked Isocyanate Curing Agent

[0070] Polyisocyanate used for preparing the blocked isocyanate curing agent of the present invention is a compound having at least two isocyanate groups in the molecular. The polyisocyanates may be aliphatic, cycloaliphatic, aromatic or aromatic-aliphatic.

[0071] Examples of the polyisocyanates include aromatic diisocyanates, such as tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), p-phenylene diisocyanate and naphthalene diisocyanate; aliphatic diisocyanates having 3 to 12 carbon atoms, such as hexamethylene diisocyanate (HDI), 2,2,4-trimethylhexane diisocyanate and lysine diisocyanate; cycloaliphatic diisocyanates having 5 to 18 carbon atoms, such as 1,4-cyclohexane diisocyanate, isophorone diisocyanate (IPDI), 4,4'-dicyclohexylmethane diisocyanate (hydrogenated MDI), methylcyclohexane

diisocyanate, isopropylidenedicyclohexyl-4,4'-diisocyanate and 1,3-diisocyanatomethylcyclohexane (hydrogenated XDI), hydrogenated TDI, 2,5- or 2,6-bis(isocyanate methyl)-bicyclo[2.2.1]heptane (=norbornane diisocyanate); aliphatic diisocyanates having aromatic ring, such as xylylene diisocyanate (XDI) and tetramethylxylylene diisocyanate (TMXDI); modified compounds thereof (urethane compound, carbodiimide, urethodion, urethonimine, biuret and/or isocyanurate modified compound); and the like. The polyisocyanate may be used alone or in combination of two or more.

[0072] Adducts or prepolymers obtained by reacting the polyisocyanate with polyalcohols such as ethylene glycol, propylene glycol, trimethylolpropane and hexanetriol at a NCO/OH ratio of not less than 2 may be used as the blocked isocyanate curing agent.

[0073] The block agent is adducted to polyisocyanate group and stable at room temperature, but free isocyanate group can be regenerated when heating it at the temperature not less than the dissociation temperature.

[0074] Pigment

[0075] The cationic electrodeposition coating composition used in the process of the present invention may contain pigment, which has been conventionally used for a coating. Examples of the pigments include inorganic pigments, for example, a coloring pigment, such as titanium dioxide, carbon black and colcothar; an extender pigment, such as kaolin, talc, aluminum silicate, calcium carbonate, mica and clay; a rust preventive pigment, such as zinc phosphorate, iron phosphorate, aluminum phosphorate, calcium phosphorate, zinc phosphite, zinc cyanide, zinc oxide, aluminum tripolyphosphate, zinc molybdate, aluminum molybdate, calcium molybdate, aluminum phosphomolybdate and aluminum zinc phosphomolybdate.

[0076] When the pigment is used as a component of the electrodeposition coating, the pigment is generally pre-dispersed in an aqueous solvent at high concentration in the form of a paste (pigment dispersed paste). This is because it is difficult to uniformly disperse the pigment, which is powdery, at low concentration in one step. The paste is generally called as pigment dispersed paste.

[0077] The pigment dispersing paste is prepared by dispersing the pigment together with pigment dispersing resin varnish in an aqueous medium. As the pigment dispersing resin, cationic or non-ionic low molecular weight surfactant, or cationic polymer such as modified epoxy resin having quaternary ammonium group and/or tertiary sulfonium group can be used. As the aqueous medium, deionized water or water containing a small amount of alcohol can be used. The pigment dispersing resin is generally used at the solid content of 20 to 100 parts by mass based on 100 parts by mass of the coating. The pigment dispersing paste can be obtained by mixing the pigment dispersing resin varnish with the pigment, and dispersing the pigment using a suitable dispersing apparatus, such as a ball mill or sand grind mill.

[0078] The cationic electrodeposition coating composition may optionally contain dissociation catalyst, organic tin compounds, such as dibutyltin dilaurate, dibutyltin oxide, dioctyltin oxide; amines, such as N-methyl morpholine; lead acetate; metal salts of strontium, cobalt and copper; in order

to dissociate the block agent in addition to the above components. The amount of the dissociation catalyst is from 0.1 to 6 parts by mass based on 100 parts by mass of the total solid content of the cationic epoxy resin and blocked isocyanate curing agent in the cationic electrodeposition coating composition.

[0079] Preparation and Application of Cationic Electrodeposition Coating Composition

[0080] The cationic electrodeposition coating composition of the present invention is prepared by dispersing the above catalyst, cationic epoxy resin, blocked isocyanate curing agent, and pigment dispersed paste in an aqueous solvent. In addition, the aqueous medium may contain a neutralizing acid in order to neutralize the cationic epoxy resin to improve the dispersibility of binder resin emulsion. Examples of the neutralizing acid include inorganic acids or organic acids, such as hydrochloric acid, nitric acid, phosphoric acid, formic acid, acetic acid, lactic acid.

[0081] The amount of the neutralizing acid is preferably from 10 mg equivalent to 25 mg equivalent, based on 100 g of the binder resin containing the cationic epoxy resin and blocked isocyanate curing agent. The lower limit of the amount of the neutralizing acid is more preferably 15 mg equivalent and the upper limit is more preferably 20 mg equivalent. When the amount of the neutralizing acid is smaller than 10 mg equivalent, the miscibility with water is not sufficiently obtained, and it is difficult to disperse in water, or the stability is greatly degraded. On the other hand, when the amount of the neutralizing acid is larger than 25 mg equivalent, the electric power necessary to deposition increases, and the deposition of the solid content of the coating is degraded, which degrades the throwing power.

[0082] The cationic electrodeposition coating composition can be prepared by dispersing the cationic epoxy resin and blocked isocyanate curing agent in an aqueous solvent. It is desired for the amount of the blocked isocyanate curing agent to be sufficient to react with activated hydrogen containing functional group, such as primary amino group, secondary amino group, and hydroxyl group during curing to provide good cured coated film. The amount of the blocked isocyanate curing agent, which is represented by a solid content ratio of the cationic epoxy resin to the blocked isocyanate curing agent (cationic epoxy resin/curing agent), is within the range of preferably 90/10 to 50/50, more preferably 80/20 to 60/40, most preferably 80/20 to 65/35. The flowability and curing rate of the coated film at the time of film forming (deposited film) are improved by adjusting the ratio, and the smoothness of the coated film is improved. The smoothness of the electrodeposition coated film is further improved by using surface treated steel plate having smaller roughness. In addition, it is easy to impart the cured electrodeposition coated film to the desired dynamic Tg and crosslinking density by adjusting the amount of the blocked isocyanate curing agent to the above range or selecting the baking temperature.

[0083] The organic solvent is used as a solvent when synthesizing resin components, such as the cationic epoxy resin, blocked isocyanate curing agent, pigment dispersing resin. The complicated procedure is necessary for com-

pletely removing the solvent. The flowability of the coated film at the time of film forming is improved by containing the organic solvent in the binder resin, and the smoothness of the coated film is improved.

[0084] Examples of the organic solvents used in the cationic electrodeposition coating composition include ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, ethylene glycol monoethylhexyl ether, propylene glycol monobutyl ether, dipropylene glycol monobutyl ether, propylene glycol monophenyl ether and the like.

[0085] The cationic electrodeposition coating composition can contain additives for a coating, such as a plasticizer, surfactant, antioxidant and ultraviolet absorber, in addition to the above components. The cationic electrodeposition coating composition may contain amino group containing acrylic resin, amino group containing polyester resin and the like.

[0086] Electrodeposition coating is carried out by applying a voltage of usually 50 to 450 V between the substrate serving as cathode and anode. When the applied voltage is lower than 50 V, the electrodeposition becomes insufficient. On the other hand, when the applied voltage is higher than 450 V, the coated film may be broken and appearance thereof becomes unusual. The electrodeposition bath temperature is usually controlled at 10 to 45° C.

[0087] The electrodeposition process comprises the steps of immersing a substrate to be coated in an electrodeposition coating composition, and applying a voltage between the substrate as cathode and anode to cause deposition of coated film. Also, the period of time for applying the voltage can be generally 2 to 4 minutes, though it varies with the electrodeposition condition.

[0088] The thickness of the electrodeposition coated film is preferably 5 to 25 μm , more preferably 20 μm . When the thickness is smaller than 5 μm , rust resistance is not sufficiently obtained. On the other hand, when the thickness is larger than 25 μm , it leads waste of the coating composition.

[0089] The electrodeposition coated film obtained in the manner as described above is baked at a temperature of 120 to 260° C., preferably 140 to 220° C. for 10 to 30 minutes to be cured directly or after being washed with water after completion of the electrodeposition process, thereby the cured electrodeposition coated film is formed.

[0090] Intermediate Coating Composition

[0091] The intermediate coating composition used in the present invention contains an intermediate coating resin component, pigment, aqueous medium and/or organic solvent. The intermediate coating resin component comprises an intermediate coating resin and optionally an intermediate coating curing agent. The aqueous medium and organic solvent can be the same as used in the cationic electrodeposition coating composition.

[0092] Examples of the intermediate coating resins include acrylic resin, polyester resin, polyurethane resin, alkyd resin, fluorine resin, epoxy resin, polyether resin and the like. Preferred are acrylic resin, polyester resin and polyurethane resin. The intermediate coating resin may be used alone or in combination with two or more.

[0093] Examples of the acrylic resins include copolymer of acrylic monomer and the other ethylenically unsaturated

monomer. Examples of the acrylic monomers, which can be used in the copolymer, include methyl ester, ethyl ester, propyl ester, n-butyl ester i-butyl ester, t-butyl ester, 2-ethylhexyl ester, lauryl ester, phenyl ester, benzyl ester and 2-hydroxypropyl ester of acrylic acid or methacrylic acid; ring opening addition product of caprolactone of 2-hydroxyethyl acrylate or methacrylate; glycidyl acrylate, glycidyl methacrylate, acrylamide, methacrylamide and N-methylol acrylamide, (meth)acrylic ester of polyalcohol and the like. Examples of the other ethylenically unsaturated monomers, which can copolymerize with the above monomer, include styrene, α -methylstyrene, itaconic acid, maleic acid, vinyl acetate and the like.

[0094] Example of the polyester resins include saturated polyester resins or unsaturated polyester resins, for examples, condensates obtained by condensing polybasic acid and polyalcohol with applied heat. Examples of the polybasic acids include saturated polybasic acids and unsaturated polybasic acids. Examples of the saturated polybasic acids include succinic acid, adipic acid, azelaic acid, sebacic acid, hexahydrophthalic acid and 1,4-cyclohexane dicarboxylic acid. Examples of the unsaturated polybasic acids include maleic acid, maleic anhydride, fumaric acid, phthalic anhydride, terephthalic acid and isophthalic acid. Examples of polyalcohols include divalent alcohols and trivalent alcohols. Examples of the divalent alcohols include ethylene glycol, diethylene glycol, neopentyl glycol, 1,5-pentanediol and 1,6-hexanediol. Examples of the trivalent alcohols include glycerin and trimethylolpropane.

[0095] Examples of the polyurethane resins include resins having urethane bond obtained from polyols components of acrylic, polyester, polyether, polycarbonate and the like and polyisocyanate compounds. Examples of the polyisocyanate compounds include 2,4-tolylene diisocyanate (2,4-TDI), 2,6-tolylene diisocyanate (2,6-TDI) and the mixture thereof (TDI), diphenylmethane-4,4'-diisocyanate (4,4'-MDI), diphenylmethane-2,4'-diisocyanate (2,4'-MDI) and the mixture thereof (MDI), naphthalene-1,5-diisocyanate (NDI), 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), xylylene diisocyanate (XDI), dicyclohexylmethane diisocyanate (hydrogenated MDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), hydrogenated xylylene diisocyanate (HXDI) and the like.

[0096] Examples of the alkyd resins include alkyd resins obtained by reacting the polybasic acid and polyalcohol with modifiers, such as fats and oils or fatty acid thereof (such as soybean oil, linseed oil, coconut oil, stearic acid and the like), natural resin (such as rosin, amber and the like).

[0097] Examples of the fluorine resins include vinylidene fluoride resin, tetrafluoroethylene resin, or the mixture thereof, fluorine-based copolymer obtained by copolymerizing fluoroolefin and monomers comprising hydroxyl group containing compound and the other copolymerizable vinyl-based compound.

[0098] Examples of the epoxy resins include resins obtained by the reaction of bisphenol with epichlorohydrin and the like. Examples of the bisphenols include bisphenol A and bisphenol F. Examples of the bisphenol type epoxy resins include Epikote 828, Epikote 1001, Epikote 1004, Epikote 1007, Epikote 1009 (which are commercially available from Shell Chemical Co.). In addition, the resins may be chain-lengthened by a suitable chain extender.

[0099] Examples of the polyether resins, which are polymer or copolymers having ether bond, include polyoxyethylene-based polyether, polyoxypropylene-based polyether or polyoxybutylene polyether, or polyether resin having at least two hydroxyl groups in one molecular, such as polyethers derived from aromatic polyhydroxy compounds, such as bisphenol A or bisphenol F. In addition, the examples also include carboxyl group containing polyether resins obtained by the reaction of the polyether resins and reactive derivatives, such as polyvalent carboxylic acid including succinic acid, adipic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid and trimellitic acid or anhydrides thereof.

[0100] It is desired for the intermediate coating resin to have an acid value of 3 to 200, a hydroxyl number of 30 to 200 and a number average molecular weight of 500 to 50,000. The preferred resins are particularly acrylic resin having an acid value of 3 to 200, a hydroxyl number of 30 to 200 and a number average molecular weight of 2,000 to 50,000 and polyester resin having an acid value of 3 to 200, a hydroxyl number of 30 to 200 and a number average molecular weight of 500 to 20,000. In the case of preparing the intermediate coating composition as an aqueous solution or aqueous dispersion, it is desired for the intermediate coating resin to have an acid value of 10 to 200 and a hydroxyl number of 30 to 200.

[0101] In the intermediate coating resins, there is generally a curable type and lacquer type resins. Preferred is the curable type. If using the curable type, an intermediate coating curing agent, such as a blocked isocyanate compound, oxazolidone compound, carbodiimide compound and melamine compound is used in combination with the intermediate coating resin. The curing reaction of the intermediate coating resin component containing the intermediate coating curing agent can be advanced under heating or at room temperature. In addition, the combination of the curable type and non-curable type intermediate coating resins can be used.

[0102] If containing the intermediate coating curing agent, a weight ratio of the intermediate coating resin to the intermediate coating curing agent in the coating solid content is preferably 90/10 to 50/50, more preferably 85/15 to 60/40. When the ratio is larger than 90/10 and the amount of the intermediate coating curing agent is smaller than 10% by weight, the crosslinking in the coated film is not sufficiently obtained. On the other hand, when the ratio is smaller than 50/50 and the amount of the intermediate coating curing agent is larger than 50% by weight, the storage stability of the coating composition is degraded and the curing rate is large, and the appearance of the coated film is degraded.

[0103] The intermediate coating composition of the present invention contains a pigment. Examples of the pigments include extender pigments, such as baryta powder, precipitated sulfate, barium carbonate, gypsum, clay, silica, talc, magnesium carbonate, alumina white and the like, and coloring pigments. Examples of the coloring pigments include organic pigments, such as azo lake-based pigment, phthalocyanine-based pigment, indigo-based pigment, perylene-based pigment, quinophthalone-based pigment, dioxazine-based pigment, quinacridone-based pigment, isoindolinone-based pigment, metal complex pigment, carbon black; or inorganic pigments, such as yellow lead,

yellow iron oxide, colcothar, titanium dioxide. The amount of the pigment can be optionally selected depending on the desired performance and hue. The pigment may be used alone or in combination with two or more.

[0104] The concentration of the pigment (PWC) based on the coating solid content of the intermediate coating composition is within the range of preferably 10 to 50% by weight. The upper limit of the concentration is more preferably 30% by weight.

[0105] The solid content of the intermediate coating composition is within the range of preferably 35 to 65% by weight. The lower limit is more preferably 40% by weight and the upper limit is more preferably 60% by weight. When the lower limit of the solid content is smaller than 35% by weight, sag occurs during the application of the coating, and the finished appearance is degraded. On the other hand, when the upper limit is larger than 65% by weight, the flowability during the application of the coating is reduced, and the finished appearance is degraded.

[0106] The intermediate coating composition can contain polyamide wax, which is lubricant dispersion of aliphatic amide, polyethylene wax, which is colloidal dispersion based on polyethylene oxide, curing catalyst, ultraviolet absorber, antioxidant, leveling agent, surface conditioner such as silicone and organic polymer, anti-sag agent, thickening agent, defoaming agent, lubricant, crosslinkable polymer powder (micro gel) and the like in addition to the above components. The performance of the coating composition and coated film can be improved by compounding the above additive in amount of not more than 15 parts by mass (based on solid content), based on 100 parts by mass of the intermediate coating resin.

[0107] Preparation and Application of Intermediate Coating Composition

[0108] The intermediate coating composition can be prepared by dissolving or dispersing the above components in a solvent. The solvent is not limited as long as it can dissolve and disperse the intermediate coating resin component, but may be organic solvent and/or water. The organic solvent may be one, which has been conventionally used in the art of the coating composition. Examples of the organic solvents include hydrocarbons such as toluene and xylene, ketones such as acetone and methyl ethyl ketone, esters such as ethyl acetate, butyl acetate, cellosolve acetate and butyl cellosolve, alcohols and the like. If it is restrained to use the organic solvent in view of circumstance, it is desired to use water. If so, a proper amount of hydrophilic organic solvent may be contained therein.

[0109] The viscosity of the intermediate coating composition during the application thereof is adjusted to preferably 10 to 30 seconds (ford cup #4/20° C.) using the organic solvent and/or water, and the mixture thereof. When the viscosity is lower than the above range, the intermediate coated film is miscible with the base top coated film formed in the subsequent applying step. On the other hand, when the viscosity is higher than the above range, it is difficult to handle the coating composition and the coated film is early solidified, and the surface evenness occurs in such a level that it can not be coated and repaired by the coated film in the subsequent coating step.

[0110] The intermediate coated film is obtained by applying the intermediate coating composition on the cured

electrodeposition coated film. The opacifying properties of the electrodeposition coated film by forming the intermediate coated film, the chipping resistance are imparted. In addition, the adhesion to the base top coated film applied on the intermediate coated film in the subsequent step is also improved.

[0111] A method of applying the intermediate coating is not limited, but it is conducted by using an air electrostatic spray coater, which is so-called "react gun"; a rotary spray electrostatic coater, which is so-called "micro micro ($\mu\mu$) bell", "micro (μ) bell", and "meta bell"; and the like. Preferred is the method by the rotary spray electrostatic coater.

[0112] It is desired for the intermediate coated film to have a dry thickness of 5 to 80 μm , preferably 10 to 50 μm . After the formation of the intermediate coated film, the step of forming the base top coated film is conducted without heating and curing. The intermediate coated film may be preheated at a temperature lower than that of heating and curing (baking) treatment before forming the base top coated film.

[0113] Base Top Coating Composition

[0114] The base top coating composition used in the present invention is brilliant coating composition or solid coating composition containing a base top coating resin component, brilliant pigment and/or coloring pigment, extender pigment and solvent. The base top coating composition is water-based or organic solvent-based including water-dispersed or organic solvent-dispersed.

[0115] The base top coating resin component contained in the base top coating composition comprises a base top coating resin and optionally a base top coating curing agent. The base top coating resin component (the base top coating resin and base top coating curing agent), coloring pigment, extender pigment, various additives and solvents contained in the base top coating composition may be the same as described in the intermediate coating. By using the base top coating resin component, the brilliant pigment and optionally the coloring pigment are dispersed in the brilliant base top coating composition and the coloring pigment are dispersed in the solid base top coating composition.

[0116] Examples of the base top coating resin used may include at least one of coated film forming resin selected from the group consisting of acrylic resin, polyester resin, fluorine resin, epoxy resin, polyurethane resin, polyether resin and the modified resins thereof. Examples of the base top coating curing agents include the intermediate coating curing agents as described above. Preferred is melamine compound, particularly etherified melamine resin. The etherified melamine resin is obtained by etherifying a melamine by alcohols, such as methanol and butanol. The preferred combination of the base top coating resin and base top coating curing agent as the base top coating resin component includes acrylic resin-melamine resin system. In the system, it is desired for the acrylic resin to have an acid value of 10 to 200, a hydroxyl number of 30 to 200 and a number average molecular weight of 2,000 to 50,000.

[0117] Examples of the brilliant pigments as the pigment contained in the base top coating composition include aluminum flake pigment, colored aluminum flake pigment, interference mica pigment, colored mica pigment, metal

oxide coated glass flake pigment, metal plated glass flake pigment, metal oxide coated silica flake pigment, metallic titanium flake pigment, graphite pigment, stainless steel flake pigment, platy iron oxide pigment, phthalocyanine flake pigment and hologram pigment. If using the brilliant pigment and/or coloring pigment, a weight content of the all pigments (PWC) is within the range of preferably 1 to 50%, more preferably 5 to 30%. When the PWC is smaller than 1%, it is not sufficient to add design to the coated film. On the other hand, the PWC is larger than 50%, the appearance of the coated film is degraded.

[0118] Preparation and Application of Base Top Coating Composition

[0119] The base top coating composition is prepared by dissolving or dispersing the above components in a solvent. The solvent is not limited as long as it can dissolve and disperse the base top coating resin component, but may be organic solvent and/or water. Examples of the organic solvents include hydrocarbons such as toluene and xylene, ketones such as acetone and methyl ethyl ketone, esters such as ethyl acetate, butyl acetate, cellosolve acetate and butyl cellosolve, alcohols and the like.

[0120] The viscosity of the base top coating composition is preferably adjusted to the range of 10 to 30 seconds (ford cup #4/20° C.) using a suitable diluent. When the viscosity is lower than the above range, the base top coated film is miscible with the clear top coated film formed in the subsequent applying step. On the other hand, when the viscosity is higher than the above range, it is difficult to handle the coating composition and the coated film is early solidified, and the surface evenness occurs in such a level that it can not be coated and repaired by the coated film in the subsequent coating step.

[0121] The base top coated film is obtained by applying the base top coating composition on the intermediate coated film. The base top coating composition is applied on the uncured intermediate coated film by wet on wet coating. The method of applying the base top coating composition is not limited, but includes the method described as the method of applying the intermediate coating composition. When the base top coating composition is applied on an automobile body, it is conducted by multi-stage coating, preferably two-stage coating with an air electrostatic spray coater in order to impart the coated film to high elegance. The applying method may be also the combination of an air electrostatic spray coater and rotary spray type electrostatic coater.

[0122] The formation of the base top coated film allows to add design to the coated film, assures the adhesion to the intermediate coated film formed in the previous step and assures the adhesion to the base top coated film coated in the subsequent step.

[0123] It is desired for the base top coated film to have a dry thickness of 5 to 50 μm , preferably 10 to 30 μm , per one coating. After the formation of the base top coated film, the subsequent step of forming the clear top coated film is conducted without heating and curing. The base top coated film may be preheated at a temperature lower than that of heating and curing (baking) treatment before forming the clear top coated film.

[0124] Clear Top Coating Composition

[0125] The clear top coating composition is formed from a clear coating composition containing a clear top coating resin component, various additives and solvents. The clear top coating composition is water-based or organic solvent-based including water-dispersed or organic solvent-dispersed.

[0126] The clear top coating resin component contained in the clear top coating composition comprises a clear top coating resin and optionally a clear top coating curing agent. The clear top coating resin component (the clear top coating resin and clear top coating curing agent), various additives and solvents contained in the clear top coating composition may be the same as described in the intermediate coating.

[0127] The preferred combination of the clear top coating resin and clear top coating curing agent as the clear top coating resin component includes acrylic resin-melamine resin system. In the system, it is desired for the acrylic resin to have an acid value of 10 to 200, a hydroxyl number of 30 to 200 and a number average molecular weight of 2,000 to 50,000.

[0128] As the clear top coating composition, a clear coating composition comprising carboxyl group containing polymer and epoxy group containing polymer disclosed in Japanese Patent Kokoku Publication No. 19315/1996 can be suitably used in order to assure the acid rain resistance and maintain the orientation of the brilliant pigment in the base top coated film by increasing the solubility difference from the base top coated film in wet on wet coating. The clear top coating composition can optionally contain additives, such as coloring pigment, extender pigment, modifier, ultraviolet absorber, leveling agent, dispersant and defoaming agent.

[0129] Preparation and Application of Clear Top Coating Composition

[0130] The clear top coating composition is prepared by dissolving or dispersing the above components in a solvent. The optional solvent described above can be used. The clear top coated film is obtained by applying the clear top coating composition on the base top coated film. The clear top coating composition is applied on the uncured base top coated film by wet on wet coating.

[0131] The method of forming the clear top coated film is not limited, but preferably includes spraying method, roll coater method and the like. It is desired for the clear top coated film to have a dry thickness of 20 to 50 μm , preferably 25 to 40 μm , per one coating.

[0132] The formation of the clear top coated film allows to protect the base top coated film and add depth feeling to the resulting multi layered coated film.

[0133] Baking

[0134] After the formation of the clear top coated film, the three layers of coated films of the uncured intermediate coated film, base top coated film and clear top coated film are baked and cured at 120 to 160° C. for a given time to obtain the multi layered coated film. In the method of the present invention, the intermediate coating composition, base top coating composition and clear top coating composition are applied in the order respectively by wet and wet coating. That is, uncured coated films are formed in order of

precedence. The term “uncured” as used herein refers to the state that the coated film does not completely cured, and includes the state of preheated coated film. The term “pre-heat” as used herein refers to leaving or heating the coated film at a temperature of room temperature to 100° C. as the temperature lower than that of heating and curing (baking) treatment for 1 to 10 minutes. The coated film having better finished appearance can be obtained by preheating the coated film after the formation of the intermediate coated film and the formation of the base top coated film respectively.

EXAMPLES

[0135] The present invention will be further explained in detail in accordance with the following examples, however, the present invention is not limited to these examples. In the examples, “part” is based on weight unless otherwise specified.

Preparation Example 1**[0136] Preparation of Amine Modified Epoxy Resin**

[0137] 92 parts of 2,4-/2,6-tolylenediisocyanate (weight ratio=8/2), 95 parts of methyl isobutyl ketone (hereinafter, referred to as MIBK) and 0.5 part of dibutyltin dilaurate were loaded to a flask equipped with a stirrer, a cooling tube, a nitrogen introducing tube, a thermometer and a dropping funnel. 21 parts of methanol was added while stirring the reaction mixture. Starting at room temperature, the reaction mixture was allowed to rise to 60° C. by exothermic, the reaction was retained for 30 minutes, and 50 parts of ethylene glycol mono-2-ethylhexyl ether was dropped from the dropping funnel. Furthermore, 53 parts of bisphenol A-propylene oxide 5 mol adduct was added. The reaction was carried out mainly in the temperature range of 60 to 65° C., and continued until absorption based on an isocyanate group disappeared in IR spectrum measurement.

[0138] Next, 365 parts of epoxy resin of epoxy equivalent 188 synthesized from bisphenol A and epichlorohydrin in accordance with a known method was added to the reaction mixture and heated to 125° C. After that, 1.0 part of benzyldimethylamine was added and allowed to react at 130° C. until epoxy equivalent became 410.

[0139] Subsequently, 61 parts of bisphenol A and 33 parts of octylic acid were added and allowed to react at 120° C. to achieve epoxy equivalent of 1190. Thereafter, the reaction mixture was cooled, and 11 parts of diethanolamine, 24 parts of N-ethylethanolamine and 25 parts of 79% by weight solution in MIBK of ketimined aminoethyl ethanolamine were added, and was allowed to react for 2 hours at 110° C. Then, the reaction mixture was diluted with MIBK until nonvolatile solid content became 80%, and an amine modified epoxy resin having a glass transition temperature of 2° C. (resin solid content: 80%) was obtained.

Preparation example 2**[0140] Preparation of Block Polyisocyanate Curing Agent (1)**

[0141] 1250 parts of diphenylmethane diisocyanate, 266.4 parts of MIBK were loaded to a reaction vessel, and 2.5 parts of dibutyltin dilaurate were added thereto after heating to 80° C. A solution of 226 parts of ϵ -caprolactam dissolved in 944 parts of butylcellsolve was dropped thereto at 80° C. over 2 hours. The reaction was retained at 100° C. for 4

hours, it was confirmed that absorption based on an isocyanate group disappeared in IR spectrum measurement, and left to be cooled. 336.1 parts of MIBK were added and thereby, a blocked isocyanate curing agent having a glass transition temperature of 0° C. was obtained.

Preparation Example 3

[0142] Preparation of Pigment Dispersing Resin

[0143] 222.0 parts of isophorone diisocyanate (hereinafter, referred to as IPDI) was loaded in a reaction vessel equipped with a stirrer, a cooling tube, a nitrogen introducing tube and a thermometer, and after diluted with 39.1 parts of MIBK, 0.2 part of dibutyltin dilaurate was added. Then, the reaction mixture was heated to 50° C., and 131.5 parts of 2-ethyl hexanol was dropped under dry nitrogen atmosphere over 2 hours with stirring. Reaction temperature was kept at 50° C. by cooling as necessary. As the result, 2-ethyl hexanol half blocked IPDI (resin solid content: 90.0%) was obtained.

[0144] 87.2 parts of dimethylethanolamine, 117.6 parts of 75% aqueous solution of lactic acid, and 39.2 parts of ethylene glycol monobutyl ether were added to a suitable reaction vessel, the reaction mixture was stirred at 65° C. for half an hour to prepare a quaternarizing agent.

[0145] Subsequently 710.0 parts of EPON 829 (bisphenol A type epoxy resin manufactured by Shell Chemical Company, epoxy equivalent 193 to 203), and 289.6 parts of bisphenol A were loaded to a reaction vessel. The reaction mixture was heated to 150 to 160° C. under nitrogen atmosphere, initial exothermic reaction was occurred. Heating was continued at 150 to 160° C. for about 1 hour, the reaction mixture was then cooled to 120° C., 498.8 parts of the prepared 2-ethyl hexanol half-blocked IPDI (MIBK solution) was added.

[0146] The reaction mixture was held at 110 to 120° C. for about 1 hour, 463.4 parts of ethylene glycol monobutyl ether were added, the mixture was cooled to 85 to 95° C., homogenized, and 196.7 parts of the prepared quaternarizing agent was added thereto. The reaction mixture was held at 85 to 95° C. until the acid value became 1, 964 parts of deionized water were added to finalize quaternarization of an epoxy-bisphenol A resin and to obtain a pigment dispersing resin having quaternary ammonium salt moiety (resin Tg=5° C., resin solid content: 50%).

Preparation Example 4

[0147] Preparation of Pigment Dispersion Paste

[0148] 120 parts of the pigment dispersing resin obtained in Preparation example 3, 2.0 parts of carbon black, 100.0 parts of kaolin, 80.0 parts of titanium dioxide, 18.0 parts of aluminum phosphomolibdate and 221.7 parts of ion-exchange water were loaded into a sand grinding mill, and they were dispersed until particle size was not more than 10 μ m, to obtain a pigment dispersion paste (solid content: 48%).

Example 1

Preparation of Cationic Electrodeposition Coating Composition and Formation of Electrodeposition Coated Film

[0149] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent

obtained in Preparation example 2 were uniformly mixed in solid content ratio of 80/20. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0150] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20.0% by weight was obtained. Tg of the electrodeposition coated film (deposited film) determined by the calculation from each resin Tg of all resin components in this electrodeposition coating composition was 15° C. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the coating composition on a surface-treated steel plate having a surface roughness Ra=0.90 μ m (cutoff value: 2.5 mm) at the electrodeposition bath temperature of 30° C. so that the electrodeposition coated film after baking had a dry thickness of 15 μ m to obtain a cationic electrodeposition coated film (A-1).

[0151] Formation of Cured Electrodeposition Coated Film

[0152] The resulting cationic electrodeposition coated film (A-1) was baked at 170° C. for 20 minutes to obtain a cured electrodeposition coated film as a substrate.

[0153] Formation of Intermediate Coated Film

[0154] Polyester-melamine cured type intermediate coating composition ("OTO H-880", commercially available from Nippon Paint Co., Ltd.) was applied on the substrate using rotary aeration type electrostatic coating apparatus so that a dry thickness was 20 μ m, preheated at room temperature for 8 minutes after applying to form an uncured intermediate coated film.

[0155] Formation of Base Top Coated Film and Clear Top Coated Film

[0156] Acryl-melamine cured type base top coating composition ("OTO H-600", commercially available from Nippon Paint Co., Ltd.) was applied on the intermediate coated film so that a dry thickness was 10 μ m, and preheated at room temperature for 7 minutes after applying to form an uncured base top coated film. Then, Acrylic acid-epoxy cured type clear top coating composition ("MAC 0-1600", commercially available from Nippon Paint Co., Ltd.) was applied on the base top coated film so that a dry thickness was 35 μ m. The intermediate coated film, the base top coated film and the clear top coated film applied were baked at 140° C. for 30 minutes to obtain a multi layered coated film.

[0157] Measurement of Centerline Average Roughness of Roughness Curve (Ra) and Centerline Average Roughness of Profile Curve (Pa)

[0158] The Ra value and Pa value of the cured electrodeposition coated film obtained from the electrodeposition coating composition were measured using an evaluation type surface roughness tester manufactured by Mitutoyo Corporation according to JIS-B 0601. The measurement was

conducted seven times using a sample comprising cutoff of 2.5 mm width, and Ra value and Pa value determined from an average obtained by removing the upper and lower values. The results are shown in Table 1.

[0159] Measurement of Surface Energy

[0160] The contact angle between the cured electrodeposition coated film of Examples and Comparative Examples, and DIW (deionized water), ethylene glycol and methylene iodide using an auto contact angle meter (PD-X type, manufactured by Kyowa Interface Science Co., Ltd.) after 30 seconds from dropping the droplet of the solvents. The surface energy of the cured electrodeposition coated film determined by the calculation from the resulting measurement values with the above equation.

[0161] Measurement of Contact Angle

[0162] The contact angle between the cured electrodeposition coated film of Examples and Comparative Examples, and the intermediate coating composition ("OTO H-880") using an auto contact angle meter (PD-X type, manufactured by Kyowa Interface Science Co., Ltd.) after 30 seconds from dropping the droplet of the intermediate coating composition.

[0163] Appearance Evaluation of Multi Layered Coated Film

[0164] The finished appearance of multi layered coated film after baking and curing was measured using a Wave-scan DOI (BYK-Gardner Co.). Among measurement values, "Wa" value has a correlation to the item of luster, "Wc" value has a correlation to the item of orange peel and "Wd" value has a correlation to the item of smoothness in the appearance of the multi layered coated film. The evaluation was conducted from the Wa, Wc and Wd values. The smaller the value is, the better the appearance is.

Example 2

[0165] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 3 were uniformly mixed in solid content ratio of 70/30. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 35, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0166] 1500 parts of this emulsion, 280 parts of the pigment dispersing resin obtained in Preparation example 4, 1560 parts of ion-exchanged water, 20 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. Tg of the electrodeposition coated film (deposited film) determined by the calculation from each resin Tg of all resin components in this electrodeposition coating composition was 14° C. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 25.5. Electrodeposition coating was conducted using the coating composition on a surface-treated steel plate having a surface roughness

Ra=0.90 μ m (cutoff value: 2.5 mm) at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film (A-2).

[0167] A multi layered coated film was obtained as described in Example 1 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 1. The results are shown in Table 1.

Example 3

[0168] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 70/30. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0169] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. Tg of the electrodeposition coated film (deposited film) determined by the calculation from each resin Tg of all resin components in this electrodeposition coating composition was 10° C. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the coating composition on a surface-treated steel plate having a surface roughness Ra=0.60 μ m (cutoff value: 2.5 mm) at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film (A-3).

[0170] A multi layered coated film was obtained as described in Example 1 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 1. The results are shown in Table 1.

Example 4

[0171] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 80/20. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0172] 1500 parts of this emulsion, 280 parts of the pigment dispersing resin obtained in Preparation example 4, 1560 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was

obtained. Tg of the electrodeposition coated film (deposited film) determined by the calculation from each resin Tg of all resin components in this electrodeposition coating composition was 15° C. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the coating composition on a surface-treated steel plate having a surface roughness Ra=0.20 μ m (cutoff value: 2.5 mm) at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film (A-4).

[0173] A multi layered coated film was obtained as described in Example 1 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 1. The results are shown in Table 1.

Example 5

[0174] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 60/40. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0175] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. Tg of the electrodeposition coated film (deposited film) determined by the calculation from each resin Tg of all resin components in this electrodeposition coating composition was 4° C. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the coating composition on a surface-treated steel plate having a surface roughness Ra=0.60 μ m (cutoff value: 2.5 mm) at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film (A-5).

[0176] A multi layered coated film was obtained as described in Example 1 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 1. The results are shown in Table 1.

Comparative Example 1

[0177] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 70/30. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for

dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0178] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. Tg of the electrodeposition coated film (deposited film) determined by the calculation from each resin Tg of all resin components in this electrodeposition coating composition was 10° C. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the coating composition on a surface-treated steel plate having a surface roughness Ra=0.90 μ m (cutoff value: 2.5 mm) at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film (B-1).

[0179] A multi layered coated film was obtained as described in Example 1 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 1. The results are shown in Table 1.

Comparative Example 2

[0180] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 70/30. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0181] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. Tg of the electrodeposition coated film (deposited film) determined by the calculation from each resin Tg of all resin components in this electrodeposition coating composition was 10° C. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the coating composition on a surface-treated steel plate having a surface roughness Ra=1.20 μ m (cutoff value: 2.5 mm) at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film (B-2).

[0182] A multi layered coated film was obtained as described in Example 1 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 1. The results are shown in Table 1.

Example 6

[0183] Preparation of Cationic Electrodeposition Coating Composition and Formation of Electrodeposition Coated Film

[0184] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 70/30. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0185] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20.0% by weight was obtained. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the resulting cationic electrodeposition coating composition at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film. The resulting deposited coated film was baked at 160° C. for 20 minutes to obtain a cured electrodeposition coated film (A-6) as a substrate.

[0186] Formation of Intermediate Coated Film

[0187] Polyester-melamine cured type intermediate coating composition ("OTO H-880", commercially available from Nippon Paint Co., Ltd.) was applied on the substrate using rotary aeration type electrostatic coating apparatus so that a dry thickness was 20 μ m, preheated at room temperature for 8 minutes after applying to form an uncured intermediate coated film.

[0188] Formation of Base Top Coated Film and Clear Top Coated Film

[0189] Acryl-melamine cured type base top coating composition ("OTO H-600", commercially available from Nippon Paint Co., Ltd.) was applied on the intermediate coated film so that a dry thickness was 10 μ m, and preheated at room temperature for 7 minutes after applying to form an uncured base top coated film. Then, Acrylic acid-epoxy cured type clear top coating composition ("MAC 0-1600", commercially available from Nippon Paint Co., Ltd.) was applied on the base top coated film so that a dry thickness was 35 μ m. The intermediate coated film, the base top coated film and the clear top coated film applied were baked at 140° C. for 30 minutes to obtain a multi layered coated film.

[0190] Measurement of Dynamic Tg of Cured Electrodeposition Coated Film

[0191] The electrodeposition coating composition prepared in Examples and Comparative Examples was electrodeposition coated on a tinplate for dynamic viscoelastic measurement to obtain an electrodeposition coated film. The electrodeposition coated film was then baked at 170° C. for 20 minutes to obtain a cured electrodeposition coated film. The resulting coated film was separated from the tinplate

using mercury and cut it to prepare a sample for the measurement. The sample was heated from room temperature to 200° C. at a raising rate of temperature of 2° C. per one minute and vibrated at a frequency of 10 Hz to measure viscoelasticity by using Rheovibron model RHEO 2000, 3000 (trade name), manufactured by Orientec Co., Ltd. A ratio ($\tan \delta$) of storage elasticity (E') to loss elasticity (E'') was calculated and its inflexion point (a temperature at a peak of $\tan \delta$) was determined to obtain a dynamic Tg.

[0192] Measurement of Crosslinking Density of Cured Electrodeposition Coated Film

[0193] The crosslinking density was determined by calculating with the resulting storage elasticity (E') obtained in the measurement of the dynamic Tg from the equation described above.

[0194] Appearance Evaluation of Multi Layered Coated Film

[0195] The finished appearance of multi layered coated film after baking and curing was measured using a Wave-scan DOI (BYK-Gardner Co.). Among measurement values, "Wa" value has a correlation to the item of luster, "Wc" value has a correlation to the item of orange peel and "Wd" value has a correlation to the item of smoothness in the appearance of the multi layered coated film. The evaluation was conducted from the Wa, Wc and Wd values. The smaller the value is, the better the appearance is.

Example 7

[0196] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 3 were uniformly mixed in solid content ratio of 80/20. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 35, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0197] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 20 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 25.5. Electrodeposition coating was conducted using the resulting cationic electrodeposition coating composition at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film. The resulting deposited coated film was baked at 160° C. for 20 minutes to obtain a cured electrodeposition coated film (A-7) as a substrate.

[0198] A multi layered coated film was obtained as described in Example 6 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 6. The results are shown in Table 2.

Example 8

[0199] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent

obtained in Preparation example 2 were uniformly mixed in solid content ratio of 80/20. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0200] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the resulting cationic electrodeposition coating composition at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film. The resulting deposited coated film was baked at 180° C. for 20 minutes to obtain a cured electrodeposition coated film (A-8) as a substrate.

[0201] A multi layered coated film was obtained as described in Example 6 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 6. The results are shown in Table 2.

Example 9

[0202] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 60/40. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0203] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the resulting cationic electrodeposition coating composition at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film. The resulting deposited coated film was baked at 180° C. for 20 minutes to obtain a cured electrodeposition coated film (A-9) as a substrate.

[0204] A multi layered coated film was obtained as described in Example 6 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 6. The results are shown in Table 2.

Comparative Example 3

[0205] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 90/10. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0206] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the resulting cationic electrodeposition coating composition at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film. The resulting deposited coated film was baked at 160° C. for 20 minutes to obtain a cured electrodeposition coated film (B-3) as a substrate.

[0207] A multi layered coated film was obtained as described in Example 6 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 6. The results are shown in Table 2.

Comparative Example 4

[0208] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 80/20. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0209] 1500 parts of this emulsion, 540 parts of the pigment dispersing resin obtained in Preparation example 4, 1920 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the resulting cationic electrodeposition coating composition at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film. The resulting deposited coated film was baked at 150° C. for 20 minutes to obtain a cured electrodeposition coated film (B-4) as a substrate.

[0210] A multi layered coated film was obtained as described in Example 6 except for the preparation of cat-

ionic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 6. The results are shown in Table 2.

Comparative Example 5

[0211] The amine-modified epoxy resin obtained in Preparation example 1 and the blocked isocyanate curing agent obtained in Preparation example 2 were uniformly mixed in solid content ratio of 70/30. To the mixture glacial acetic acid was added so that milligram equivalent value of acid based on 100 g of the binder resin solid content MEQ(A) was 30, and ion-exchanged water was slowly added for dilution. MIBK was removed under reduced pressure to obtain an emulsion having a solid content of 36%.

[0212] 1500 parts of this emulsion, 280 parts of the pigment dispersing resin obtained in Preparation example 4, 1560 parts of ion-exchanged water, 40 parts of 10% cerium acetate aqueous solution, and 10 parts of dibutyltin oxide were mixed, and a cationic electrodeposition coating composition having a solid content of 20% by weight was obtained. The electrodeposition coating composition had a volatile organic content in the coating (VOC) of 0.5%, and a milligram equivalent value of acid based on 100 g of the resin solid content (MEQ(A)) of 24.2. Electrodeposition coating was conducted using the resulting cationic electrodeposition coating composition at the electrodeposition bath temperature of 30° C. to obtain a cationic electrodeposition coated film. The resulting deposited coated film was baked at 180° C. for 20 minutes to obtain a cured electrodeposition coated film (B-S) as a substrate.

[0213] A multi layered coated film was obtained as described in Example 6 except for the preparation of cationic electrodeposition coating composition and formation of electrodeposition coated film described above. The resulting multi layered coated film was evaluated as described in Example 6. The results are shown in Table 2.

[0214] Test Results

TABLE 1

	Example No.					Comparative Example No.	
	1 A-1	2 A-2	3 A-3	4 A-4	5 A-5	1 B-1	2 B-1
Evaluation of cured electrodeposition coated film							
Ra(μm) (Cutoff 2.5)	0.25	0.23	0.23	0.05	0.19	0.25	0.3
Pa(μm) (Cutoff 2.5)	0.3	0.24	0.28	0.05	0.21	0.34	0.44
Surface energy (mJ/m ²)	37	39	41	37	44	41	42
Contact angle to intermediate coating composition (degree)	17	20	25	17	36	32	33
Evaluation of appearance of multi layered coated film							
Wa	8	9	8	7	10	12	15
Wc	14	16	16	12	20	23	27
Wd	14	16	17	11	17	20	23

[0215]

TABLE 2

	Example No.				Comparative Example No.		
	6 A-6	7 A-7	8 A-8	9 A-9	3 B-3	4 B-4	5 B-5
Evaluation of cured electrodeposition coated film							
Cross-linking density (mmol/cc)	1.42	1.20	1.62	2.51	0.91	1.10	1.99
Dynamic Tg (° C.)	108	100	110	130	110	101	90
Evaluation of appearance of multi layered coated film							
Wa	○(8)	○(9)	○(8)	○(8)	x(12)	x(12)	x(15)
Wc	○(18)	○(17)	○(17)	○(17)	x(21)	x(21)	x(24)
Wd	○(16)	○(16)	○(16)	○(17)	x(22)	x(21)	x(22)

Wa ○: not more than 10, x: not less than 11

Wc ○: not more than 20, x: not less than 21

Wd ○: not more than 20, x: not less than 21

[0216] As is apparent from the results shown in Table 1, the cured electrodeposition coated films of the present invention of Examples 1 to 5 had good surface condition. The multi layered coated films having good appearance without appearance defects from the electrodeposition coated films were obtained by three coat one bake coating on the cured electrodeposition coated films. On the other hand, in Comparative Examples 1 to 2, since the electrodeposition coated films had appearance defects therefrom, the multi layered coated films having good appearance were not obtained.

[0217] As is apparent from the results shown in Table 2, the multi layered coated films obtained by three coat one bake coating on the cured electrodeposition coated films of the present invention of Examples 6 to 9 had good appearance. On the other hand, in Comparative Examples 3 to 5, the multi layered coated films having good appearance were not obtained.

1. A process for forming a multi layered coated film comprising the steps of:

conducting electrodeposition coating with a cationic electrodeposition coating composition on a substrate, and then heating and curing it to form an cured electrodeposition coated film on the substrate,

applying an intermediate coating composition on the cured electrodeposition coated film to form an uncured intermediate coated film,

applying a base top coating composition on the uncured intermediate coated film to form an uncured base coated film

applying a clear top coating composition on the uncured base coated film to form an uncured clear coated film, and

simultaneously heating and curing the uncured intermediate coated film, the uncured base top coated film and the uncured clear coated film; wherein

the cured electrodeposition coated film has a centerline average roughness (Ra) of 0.05 to 0.25 μm obtained from a roughness curve and a centerline average roughness (Pa) of 0.05 to 0.30 μm obtained from a profile curve.

2. A process for forming a multi layered coated film comprising the steps of:

conducting electrodeposition coating with a cationic electrodeposition coating composition on a substrate, and then heating and curing it to form an cured electrodeposition coated film on the substrate,

applying an intermediate coating composition on the cured electrodeposition coated film to form an uncured intermediate coated film,

applying a base top coating composition on the uncured intermediate coated film to form an uncured base coated film

applying a clear top coating composition on the uncured base coated film to form an uncured clear coated film, and

simultaneously heating and curing the uncured intermediate coated film, the uncured base top coated film and the uncured clear coated film; wherein

the cured electrodeposition coated film has a surface energy of 37 to 43 mJ/m^2 , and the intermediate coating composition has a contact angle of 10 to 30 degrees on the cured electrodeposition coated film.

3. A process for forming a multi layered coated film comprising the steps of:

conducting electrodeposition coating with a cationic electrodeposition coating composition on a substrate, and then heating and curing it to form an cured electrodeposition coated film on the substrate,

applying an intermediate coating composition on the cured electrodeposition coated film to form an uncured intermediate coated film,

applying a base top coating composition on the uncured intermediate coated film to form an uncured base coated film

applying a clear top coating composition on the uncured base coated film to form an uncured clear coated film, and

simultaneously heating and curing the uncured intermediate coated film, the uncured base top coated film and the uncured clear coated film; wherein

the cured electrodeposition coated film has a centerline average roughness (Ra) of 0.05 to 0.25 μm obtained from a roughness curve, a centerline average roughness (Pa) of 0.05 to 0.30 μm obtained from a profile curve and a surface energy of 37 to 43 mJ/m^2 , and the intermediate coating composition has a contact angle of 10 to 30 degrees on the cured electrodeposition coated film.

4. A process for forming a multi layered coated film comprising the steps of:

conducting electrodeposition coating with a cationic electrodeposition coating composition on a substrate, and

then heating and curing it to form an cured electrodeposition coated film on the substrate,

applying an intermediate coating composition on the cured electrodeposition coated film to form an uncured intermediate coated film,

applying a base top coating composition on the uncured intermediate coated film to form an uncured base coated film

applying a clear top coating composition on the uncured base coated film to form an uncured clear coated film, and

simultaneously heating and curing the uncured intermediate coated film, the uncured base top coated film and the uncured clear coated film; wherein

the cured electrodeposition coated film has a glass transition temperature T_g of 100 to 130° C. and a crosslinking density of 1.2 to 2.6 mmol/cc , obtained by dynamic viscoelastic measurement.

5. The process for forming a multi layered coated film according to claim 1, wherein the intermediate coating composition comprises

an intermediate coating resin comprising at least one selected from the group comprising of acrylic resin, polyester resin and polyurethane resin

an intermediate coating curing agent comprising at least one selected from the group consisting of blocked isocyanate compound, oxazoline compound, carbodiimide compound and melamine compound, and

a pigment.

6. The process for forming a multi layered coated film according to claim 2, wherein the intermediate coating composition comprises

an intermediate coating resin comprising at least one selected from the group comprising of acrylic resin, polyester resin and polyurethane resin

an intermediate coating curing agent comprising at least one selected from the group consisting of blocked isocyanate compound, oxazoline compound, carbodiimide compound and melamine compound, and

a pigment.

7. The process for forming a multi layered coated film according to claim 3, wherein the intermediate coating composition comprises

an intermediate coating resin comprising at least one selected from the group comprising of acrylic resin, polyester resin and polyurethane resin

an intermediate coating curing agent comprising at least one selected from the group consisting of blocked isocyanate compound, oxazoline compound, carbodiimide compound and melamine compound, and

a pigment.

8. The process for forming a multi layered coated film according to claim 4, wherein the intermediate coating composition comprises

an intermediate coating resin comprising at least one selected from the group comprising of acrylic resin, polyester resin and polyurethane resin

an intermediate coating curing agent comprising at least one selected from the group consisting of blocked

isocyanate compound, oxazoline compound, carbodiimide compound and melamine compound, and
a pigment.

* * * * *