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(54) **METHOD OF FORMING MULTILAYERED COATING FILM**

(57) There is disclosed a method of forming a multilayered coating film by coating a cationic electrodeposition paint, containing a blocked polyisocyanate compound as a crosslinking agent, forming an intermediate coating film by coating a water-based intermediate paint, containing a blocked polyisocyanate compound as a cross-linking agent, on the formed, electrodeposited coating film without curing said electrodeposited coating film, and then heating both coating films to form a multilayered coating film by curing both together, characterized by regulating so that the crosslinking curing reaction of said electrodeposited coating film starts earlier than the crosslinking curing reaction of said intermediate coating film. According to the method the finish appearance (smoothness, gloss etc.), interlaminar adhesion between both coating films of the multilayered coating film can be improved.

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Description**Technical Field**

5 [0001] The present invention relates to a method of forming a multilayered coating film by coating a cationic electrodeposition paint and a water-based intermediate paint by a wet-on-wet process and then by heating both coating films to cure both together through crosslinking, wherein the finish appearance (smoothness, gloss, etc.), interlaminar adhesion between both coating films, etc. of the formed multilayered coating film are improved.

10 **Background Art**

[0002] It is already known hitherto to form a multilayered coating film by coating a cationic electrodeposition paint, using blocked polyisocyanate compound as a crosslinking agent, and a water-based intermediate paint, containing polyester resin and amino resin, on an outer panel of a motorcar etc. by a wet-on-wet process and then by heating both coating films to cure both together.

[0003] This multilayered coating film, however, has not a satisfactory finish appearance such as smoothness, gloss, etc. and it has been difficult to correct these defects even by coating with a topcoat paint. Moreover, there is a problem that a peeling is prone to occur between the layers of said both coating films hit by a pebble spattered while driving.

[0004] The purpose of the present invention is to provide a method of forming a multilayered coating film excellent in the finish appearance, interlaminar adhesion, etc. while dissolving the problems as mentioned above in a multilayered coating film consisting of a cationically electrodeposited coating film and, a water-based intermediate coating film. This time, it was found that this purpose can be achieved by using a blocked polyisocyanate compound as a cross-linking agent for both of a cationic electrodeposition paint and a water-based intermediate paint and by regulating so that the cross-linking curing reaction of the electrodeposited coating film starts earlier than that of the intermediate coating film and consequently the finish appearance (smoothness, gloss, etc.), interlaminar adhesion between both coating films, etc. of the multilayered coating film are improved and the present invention has been completed.

Disclosure of the Invention

30 [0005] The present invention relates to a method of forming a multilayered coating film by coating a cationic electrodeposition paint (A), containing a blocked polyisocyanate compound as a crosslinking agent, forming an intermediate coating film by coating a water-based intermediate paint (B), containing a blocked polyisocyanate compound as a crosslinking agent, on the formed, electrodeposited coating film without curing said electrodeposited coating film, and heating both coating films to cure both together, characterized by regulating so that the crosslinking curing reaction of said electrodeposited coating film starts earlier than the crosslinking curing reaction of said intermediate coating film.

[0006] In the present specification the measurement of the starting point of the crosslinking curing of the coating films of a cationic electrodeposition paint (A) and a water-based intermediate paint (B) is conducted by using Rigid Body Pendulum Free Damping Oscillation Instrument (Toyo Bordwin Co., Ltd., Leoviblon DDV-OPA Type). Specifically a pendulum of 22 g weight and $850 \text{ g} \cdot \text{cm}^2$ moment of inertia is put on an uncured coating film, coated on a steel plate so that the film thickness would be $30 \mu\text{m}$ after curing, and said coating film is heated to the temperature prescribed for crosslinking curing (for example, $140\text{-}180^\circ\text{C}$) while oscillating the pendulum. The point when the value of logarithmic attenuation rate of the pendulum starts increasing is defined as the "starting point of crosslinking curing" and the time required from the starting of heating to the starting point of crosslinking curing is defined as "starting time of curing". If it is shorter, it means that "the crosslinking curing reaction starts earlier" The comparison of the starting point of crosslinking curing of both coating films is made based upon the results measured at the same temperature.

Description of Specific

Embodiments

50 [0007] Then the method of forming a multilayered coating film of the present invention will be described in more detail.

Cationic electrodeposition paint (A):

55 [0008] The cationic electrodeposition paint (A) used in the method of the present invention contains a blocked polyisocyanate compound as a crosslinking agent and is preferably a cationic electrodeposition paint containing a base resin (A-1), having a hydroxyl group and a cationic group, and a blocked polyisocyanate compound (A-2).

[0009] In a base resin (A-1) the hydroxyl group participates in the crosslinking reaction with a blocked polyisocyanate compound and the cationic group contributes to form a stable dispersion in water. As a base resin, for example, the followings are mentioned.

- 5 (i) A reaction product of a polyepoxy resin and a cationizing agent.
 (ii) A protonized product of a polycondensation product of a polycarboxylic acid and a polyamine (cf. U. S. Patent No. 2450940 Specification) with an acid.
 (iii) A protonized product of a polyaddition product of a polyisocyanate compound and polyol and mono- or polyamine with an acid.
 10 (iv) A protonized product of a copolymer of an acrylic type or vinyl type monomer containing hydroxyl group and amino group with an acid (cf. Japanese Patent Publication No. 12395/1970 and Japanese Patent Publication No. 12396/1970).
 (v) A protonized product of an adduct of polycarboxylic acid resin and alkyleneimine with an acid (cf. U. S. Patent No. 3403088 Specification).

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[0010] As specific examples and preparation processes of these cationic resins are described, for example, in Japanese Patent Publication No. 12395/1970, Japanese Patent Publication No. 12396/1970, Japanese Patent Publication No. 23087/1974, U. S. Patent No. 2,450,940 Specification, U. S. Patent No. 3,403,088 Specification, U. S. Patent No. 3,891,529 Specification, U. S. Patent No. 3,963,663 Specification, these quotations here replace detailed descriptions.

20 **[0011]** What is particularly preferable as base resin (A-1) is a product, which is included in the aforementioned (i) and obtained by reacting a cationizing agent to an epoxy group of a polyepoxide resin with an excellent anticorrosivity, obtained by a reaction of a polyphenol compound and epichlorohydrin.

[0012] Said polyepoxide resin is a low molecular weight or high molecular weight compound having 2 or more epoxy groups in the molecule and has suitably have a number-average molecular weight in the range of at least 200, preferably 400-4,000, more preferably 800-2,000. As such a polyepoxide resin a per se known substance can be used and there is included, for example, a polyglycidyl ether of a polyphenol compound which can be prepared by reacting a polyphenol compound with epichlorohydrin in the presence of an alkali. As a polyphenol compound usable in that case there are mentioned, for example, bis(4-hydroxyphenyl)-2,2-propane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, bis(4-hydroxyphenyl)-1,1-isobutane, bis(4-hydroxy-tert-butyl-phenyl)-2,2-propane, bis(2-hydroxybutyl)methane, 1,5-dihydroxynaphthalene, bis(2,4-dihydroxyphenyl)methane, tetra(4-hydroxyphenyl)-1,1,2,2-ethane, 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxydiphenyl sulfone, phenol novolac, cresol novolac etc.

30 **[0013]** What is particularly suitable for the preparation of a base resin (A-1) among these polyepoxide resins is a polyglycidyl ether of a polyphenol compound of a number-average molecular weight of at least about 380, preferably about 800 - about 2,000 and an epoxy equivalent of 190-2000, preferably 400-1000. This includes products obtained by partially reacted with a polyol, polyether polyol, polyester polyol, polyamidoamine, polycarboxylic acid, polyisocyanate compound etc. Further, products obtained by graft-polymerization of ϵ -caprolactone, acrylic monomer etc. are included. A reaction product of a polyepoxy resin and a cationizing agent (i) is obtained by reacting a cationizing agent to almost all or all of the epoxy groups of the above-mentioned polyepoxide resin.

35 **[0014]** As a cationizing agent there can be used, for example, amine compounds such as a primary amine, secondary amine, tertiary amine, polyamine etc. which are reacted with an epoxy group by a per se known process to introduce a cationic group such as a secondary amino group, tertiary amino group, quaternary ammonium group etc. into said polyepoxy resin and to make a resin containing a cationic group.

40 **[0015]** As a primary amine compound there can be mentioned, for example, methylamine, ethylamine, n-propylamine, isopropylamine, monoethanolamine, n-propanolamine, isopropanolamine etc. As a secondary amine compound there can be mentioned, for example, diethylamine, diethanolamine, di-n-propanolamine, diisopropanolamine, N-methylethanolamine, N-ethylethanolamine etc. As a tertiary amine compound there can be mentioned, for example, triethylamine, triethanolamine, N,N-dimethylethanolamine, N-methyldiethanolamine, N,N-diethylethanolamine, N-ethyldiethanolamine etc. As a polyamine there can be mentioned, for example, ethylenediamine, diethylenetriamine, hydroxyethylaminoethylamine, ethylaminoethylamine, methylaminopropylamine, dimethylaminoethylamine, dimethylaminopropylamine etc.

45 **[0016]** A cationic group may be obtained by protonizing with an acid a basic group formed by reacting an epoxy group of a polyepoxy resin by using as a cationizing agent other basic compounds than these amine compounds such as ammonia, hydroxylamine, hydrazine, hydroxyethylhydrazine, N-hydroxyethylimidazoline etc. As a usable acid a water-soluble organic carboxylic acid such as formic acid, acetic acid, glycolic acid, lactic acid etc. is preferable.

50 **[0017]** As a hydroxyl group such a resin containing a cationic group has there can be mentioned, for example, a primary hydroxyl group introduced by a reaction with the above-mentioned alkanolamine as a cationizing agent, by a reaction with a ring-opened product of caprolactone, which may be introduced into a polyepoxide resin, and a polyol, etc.; a secondary hydroxyl group which an epoxy resin originally has. Among these, a primary hydroxyl group intro-

duced by a reaction with an alkanolamine is preferable due to a good crosslinking reactivity with a blocked polyisocyanate compound (crosslinking agent). As such an alkanolamine those mentioned above as the above-mentioned cationizing agent are preferable.

[0018] The content of hydroxyl group in the above-mentioned base resin (A-1) is preferable as hydroxyl equivalent in the range of 20-5,000, particularly 60-3,000, more particularly 100-1,000 mgKOH/g and particularly the primary hydroxyl group equivalent is preferable in the range of 200-1,000 mgKOH/g. The content of cationic group is preferable more than the minimum amount necessary to stably disperse said base resin in water and is preferable in the range of generally 3-200, particularly 5-150, more particularly 10-80 calculated as KOH (mg/g solid content) (amine value).

[0019] It is desirable that a base resin (A-1) does not contain a free epoxy group in principle.

[0020] On the other hand, a blocked polyisocyanate compound (A-2) used as a crosslinking agent in the cationic electrodeposition paint (A) is a substance in which substantially all the isocyanate groups of a polyisocyanate compound are blocked by reacting with a volatile active hydrogen compound (blocking agent) to convert inactive at normal temperature. On heating higher than the prescribed temperature the original isocyanate group is regenerated by dissociating the blocking agent and participates in the crosslinking reaction with the base resin (A-1).

[0021] A polyisocyanate compound is a compound of an aliphatic type, alicyclic type or aromatic type having two or more free isocyanate groups in the molecule and there can be mentioned, for example, aliphatic diisocyanates such as hexamethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, dimer acid diisocyanate, lysine diisocyanate etc.; alicyclic diisocyanates such as isophorone diisocyanate, methylenebis(cyclohexylisocyanate), methylcyclohexane diisocyanate, cyclohexane diisocyanate, cyclopentane diisocyanate etc.; aromatic diisocyanates such as xylylene diisocyanate, tolylene diisocyanate, diphenylmethane diisocyanate, naphthalene diisocyanate, toluidine diisocyanate etc.; urethanized adducts, biuret type adducts, isocyanuric ring type adducts of these polyisocyanate compounds, etc.

[0022] As a blocking agent used to temporarily block the isocyanate group of the above-mentioned polyisocyanate compound there can be mentioned, for example, phenol type blocking agents such as phenol, cresol, xylenol, p-ethylphenol, o-isopropylphenol, p-tert-butylphenol, p-tert-octylphenol, thymol, p-naphthol, p-nitrophenol, p-chlorophenol etc.; alcohol type blocking agents such as methanol, ethanol, propanol, butanol, amyl alcohol, ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, propylene glycol monomethyl ether, methyl cellosolve, butyl cellosolve, methyl carbitol, benzyl alcohol, phenyl cellosolve, furfuryl alcohol, cyclohexanol, methyl glycolate, butyl glycolate, diacetone alcohol, methyl lactate, ethyl lactate etc.; active methylene type blocking agents such as acetylacetone, dimethyl malonate, diethyl malonate, ethyl acetoacetate etc.; mercaptan type blocking agents such as butyl mercaptan, hexyl mercaptan, thiophenol, methylthiophenol, ethylthiophenol, tert-dodecyl mercaptan etc.; acid amide type blocking agents such as acetanilide, acetaniside, acetamide, benzamide etc.; imide type blocking agents such as succinimide, maleimide etc.; amine type blocking agents such as diphenylamine, xylidine, dibutylamine, phenyl-naphthylamine, aniline, carbazole etc.; imidazole type blocking agents such as imidazole, 2-ethylimidazole etc.; urea type blocking agents such as urea, thiourea, ethylene urea etc.; carbamic acid type blocking agents such as phenyl N-phenylcarbamate, 2-oxazolidone etc.; imine type blocking agents such as ethyleneimine, propyleneimine etc.; oxime type blocking agents such as formamide oxime, formaldoxime, acetoaldoxime, acetoxime, methyl ethyl ketoxime, diacetyl monoxime, cyclohexanone oxime etc.; sulfurous acid type blocking agents such as sodium bisulfite, potassium bisulfite etc.; lactam type blocking agents such as ϵ -caprolactam, δ -valerolactam, γ -butyrolactam, β -propiolactam etc.

[0023] The reaction of a polyisocyanate compound and an active hydrogen compound (blocking agent) to prepare a blocked polyisocyanate compound (A-2) can be conducted by a per se known process and it is desirable that the obtained blocked polyisocyanate compound does not substantially contain a free isocyanate group.

[0024] The compounding ratio of the base resin (A-1) and the blocked polyisocyanate compound (A-2) in a cationic electrodeposition paint (A) is not particularly limited but is preferable generally upon the total solid content of said both components in the range of 40-90%, particularly 50-80% of the base resin (A-1) and 60-10%, particularly 50-20% of the blocked polyisocyanate compound (A-2).

[0025] A cationic electrodeposition paint (A) can be prepared by neutralizing the cationic group in a base resin (A-1) with an acid compound such as acetic acid, formic acid, lactic acid, phosphoric acid etc. and dispersing and mixing with a blocked polyisocyanate compound in water. The pH of the water dispersion is preferably in the range of 3-9, particularly 5-7 and the resin solid content concentration is suitably in the range of 5-30% by weight.

[0026] To a cationic electrodeposition paint (A) there can be compounded, as necessary, a curing catalyst having an anticorrosivity such as hydroxide, oxide, organic acid salt, inorganic acid salt of a metal selected from aluminium, nickel, zinc, strontium, zirconium, molybdenum, tin, antimony, lanthanum, tungsten etc.; extender pigment; color pigment; anticorrosive pigment; antisepting agent etc.

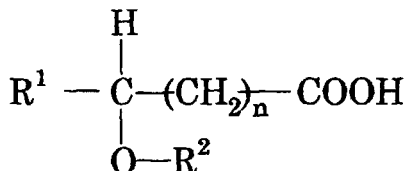
[0027] Moreover, in order to accelerate the crosslinking reaction of the base resin (A-1) and the blocked polyisocyanate compound (A-2) there can be compounded a curing catalyst such as tin octoate, dibutyltin dilaurate, manganese-containing compounds, cobalt-containing compounds, lead-containing compounds, zirconium octoate, zinc octoate,

dibutyltin bis-O-phenylphenylene, dibutyltin S,S-dibutyldithiocarbonate, triphenylantimony dichloride, dibutyltin maleate, dibutyltin diacetate, dibutyltin dilaurate mercaptide, triethylenediamine, dimethyltin dichloride etc. Its compounding ratio is suitably in the range of generally 0.1-10 parts by weight particularly 0.5-2 parts by weight per 100 parts by weight of the total amount of the base resin (A-1) and the blocked polyisocyanate compound (A-2).

5 **[0028]** Particularly, in the present invention, it is desirable to use, as a cationic electrodeposition paint (A), a lead-free cationic electrodeposition paint comprising, in addition to the aforementioned base resin (A-1) and blocked polyisocyanate compound (A-2), further a bismuth-containing compound (A-3). Thereby it becomes possible to form an electrodeposited coating film excellent in anticorrosivity and curability without using a lead compound which is problematic in environmental hygiene.

10 **[0029]** As a bismuth-containing compound compoundable in a cationic electrodeposition paint (A) there are included oxide, hydroxide, salts with an inorganic or organic acid etc. of bismuth and can be mentioned, for example, bismuth hydroxide, bismuth trioxide, bismuth nitrate, bismuth benzoate, bismuth citrate, bismuth oxycarbonate, bismuth silicate etc. Above all, bismuth hydroxide is preferable. Such a bismuth-containing compound can be compounded in the range of generally 0.1-10 parts by weight particularly 0.15-7.5 parts by weight, more particularly 0.2-5 parts by weight per 100 parts by weight of the total amount of the base resin (A-1) and the blocked polyisocyanate compound (A-2).

15 **[0030]** Moreover, as a bismuth-containing compound (A-3) there can be used a water dispersion paste of bismuth, in which an aliphatic carboxylic acid-modified bismuth compound is dispersed homogeneously and stably in a non-water-soluble form, obtained by mixing and dispersing a water-insoluble bismuth compound and an aliphatic carboxylic acid represented by the formula



25

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wherein R¹ represents a hydrogen atom or an alkyl group of carbon number 1-3; R² represents a hydrogen atom or an alkyl group of carbon number 1-10; n is 0 or 1,

35 in an aqueous medium in the presence of a dispersant, as necessary.

[0031] The above-mentioned water dispersion paste, compoundable in a cationic electrodeposition paint (A), containing non-water-soluble, aliphatic carboxylic acid-modified bismuth compound (hereinafter referred to as water dispersion paste of bismuth or simply water dispersion paste) can be prepared by mixing and dispersing a water-insoluble bismuth compound and an aliphatic carboxylic acid represented by the above-mentioned formula in an aqueous medium in the presence of a dispersant. In that case, said aliphatic carboxylic acid is used in such a ratio that a non-water-soluble aliphatic carboxylic acid-modified bismuth compound is mainly formed. Thus, a water dispersion paste of bismuth, in which the formed aliphatic carboxylic acid-modified bismuth compound is dispersed homogeneously and stably in a non-water-soluble state, is obtained. By compounding this water dispersion paste in an electrodeposition paint the curability and anticorrosivity of the electrodeposited coating film can be markedly improved without deteriorating the throwing power and finishing property at all.

45 **[0032]** The content of a water-soluble bismuth compound existing in the supernatant obtained by centrifuging (at 12000 rpm for 30 minutes) the above-mentioned water dispersion of bismuth, calculated as weight of metallic bismuth, is desirably less than about 40%, particularly less than about 30%, more particularly less than about 20% of the total amount of water-insoluble bismuth compound used as starting material.

50 **[0033]** As a water-insoluble bismuth compound used for preparing such a water dispersion paste of bismuth there are mentioned, for example, bismuth compounds, whose solubility in water at 20°C is less than 0.001 g/100 g, such as bismuth oxide, bismuth hydroxide, basic bismuth carbonate etc. Above all, bismuth oxide is preferable.

[0034] The aliphatic carboxylic acid represented by the aforementioned formula is used for the purpose of converting the above-mentioned water-insoluble bismuth compound into a sufficiently homogeneous dispersion in an aqueous medium and specifically mentioned, for example, aliphatic hydroxycarboxylic acids such as hydroxyacetic acid, lactic acid, hydroxypropionic acid etc.; aliphatic alkoxycarboxylic acids such as methoxyacetic acid, ethoxyacetic acid, 3-methoxypropionic acid etc. Among them, lactic acid, particularly L-lactic acid, and methoxyacetic acid are preferable. They can be used singly or in combination of two or more. The above-mentioned aliphatic carboxylic acids may be used

together with other organic acids, for example, acetic acid.

[0035] The application amount of the above-mentioned aliphatic carboxylic acid is in such a range that the obtained aliphatic carboxylic acid-modified bismuth compound can be in a non-water-soluble state and is different according to the kind of the aliphatic carboxylic acid to be used and can be, for example, in case of L-lactic acid, in the range of usually 0.5-1.7, preferably 0.75-1.3 as molar ratio to the bismuth amount in the water-insoluble bismuth compound, and in case of methoxyacetic acid, in the range of usually 0.25-2.5, preferably 0.5-1.3 as molar ratio to the bismuth amount in the water-insoluble bismuth compound.

[0036] As the above-mentioned dispersant cationic resins for dispersion or surface-active agents etc., which are per se known in the field of cationic electrodeposition paint, can be used without any restriction and as said cationic resins for dispersion anything selected optionally from the substances listed later as base resins for electrodeposition paint can be used. There can be mentioned, for example, resins of tertiary amine type, quaternary ammonium salt type, tertiary sulfonium salt type etc. As surface-active agents, there can be mentioned, for example, nonionic surface-active agents such as acetylene glycol type, polyethylene glycol type, polyhydric alcohol type etc. with HLB in the range of 3-18, preferably 5-15.

[0037] The application amount of the above-mentioned dispersant can be varied according to its kind, the application amount of water-insoluble bismuth compound etc. and is preferably in the range of usually 1-150 parts by weight, particularly 10-100 parts by weight per 100 parts by weight of the water-insoluble bismuth compound.

[0038] The preparation of the above-mentioned water dispersion paste of bismuth using water-insoluble bismuth compound, aliphatic carboxylic acid and dispersant can be conducted in the same manner as the preparation of a pigment paste used in a cationic electrodeposition paint. Specifically a water dispersion paste of bismuth can be prepared, for example, by adding an aliphatic carboxylic acid and water-insoluble bismuth compound in water containing dispersant and by dispersion treating in a dispersion mixer such as ball mill, sand mill etc. The obtained water dispersion paste can have a solid content concentration of generally 10-70% by weight, preferably 30-60% by weight.

[0039] Furthermore, a water dispersion paste of bismuth may be prepared as a pigment paste by adding pigments used for a usual cationic electrodeposition paint. Specifically, for example, after preparing a pigment paste by compounding a resin for pigment dispersion, neutralizing agent and pigments and by dispersion treating in a dispersion mixer such as ball mill, sand mill etc., the above-mentioned water dispersion paste of bismuth can be added to it. As a neutralizing agent used for the neutralization of the above-mentioned resin for pigment dispersion there can be used an organic acid, for example, acetic acid, formic acid, lactic acid etc.

[0040] As the above-mentioned resin for pigment dispersion, for example, anything hitherto known can be used without any restriction; for example, a cationic resin for dispersion can be used in the same manner as being used for the preparation of the above-mentioned dispersion paste of bismuth.

[0041] As the above-mentioned pigments any optional pigment, so long as a pigment usually used for an electrodeposition paint, can be used without particular restriction and there can be mentioned, for example, color pigments such as titanium oxide, carbon black, iron oxide red etc.; extender pigments such as clay, mica, baryta, talc, calcium carbonate, silica etc.; anticorrosive pigments such as aluminium phosphomolybdate, aluminium triphosphate etc.

[0042] A water dispersion paste of bismuth or a pigment paste containing said water dispersion paste can be compounded in a binder resin component etc. of a cationic electrodeposition paint.

[0043] The above-mentioned water dispersion paste of bismuth can be compounded in a cationic electrodeposition paint in such a ratio that the bismuth metal content per 100 parts by weight of the total of a base resin (A-1) and a blocked polyisocyanate compound (A-2) is in the range of generally 0.1-10 parts by weight, preferably 0.3-7 parts by weight, more preferably 0.5-5 parts by weight.

[0044] In the present invention the crosslinking curing reaction of the coating film of a cationic electrodeposition paint (A) should start earlier than the crosslinking curing reaction of the coating film of an intermediate paint (B) located on the upper layer. For that purpose, for example, it is preferable to set the curing temperature of the coating film of a cationic electrodeposition paint (A) lower compared with the curing temperature of the coating film of an intermediate paint (B). For example, The difference of curing temperature of both coating films is preferably in the range of 5-20°C, particularly 5-15°C. If the crosslinking curing reaction of the cationic electrodeposition paint (A) starts later than that of the intermediate paint, it is generally difficult to improve the finish appearance (smoothness, gloss, etc.) of the multilayered coating film, interlaminar adhesion between both coating films, etc.

[0045] The starting point of the crosslinking curing reaction of the coating film of cationic electrodeposition paint (A) can be easily regulated, for example, by suitably selecting the kind, compounding amount etc. of polyisocyanate compound, blocking agent, curing catalyst etc.

[0046] Concerning the coating film of a cationic electrodeposition paint (A), the "starting time of curing" from the start of heating to the starting point of the crosslinking curing is suitably between 5-15 minutes in the coating procedure.

[0047] The coating of a cationic electrodeposition paint (A) is preferably conducted, for example, by using the substrate as cathode and a carbon plate as anode under the condition of bath temperature 20-35°C, voltage 100-400V, current density 0.01-5A, conducting time 1-10 minutes. The coating film thickness can be made about 10 - about 40 μm as

cured coating film. As a substrate, for example, material having electroconductive metal surface, particularly motorcar body, electric appliances etc. are mentioned.

[0048] In the method of the present invention, after coating of the cationic electrodeposition paint (A), a water-based intermediate paint (B), containing a blocked polyisocyanate compound as crosslinking agent is coated on its coating surface without curing its coating film.

Water-based intermediate paint (B):

[0049] Water-based intermediate paint (B) is a water-based paint containing a blocked polyisocyanate compound as a crosslinking agent and preferably a water-based paint obtained by containing a base resin (B-1) having a functional group crosslinkable with an isocyanate group such as a hydroxyl group etc. and a blocked polyisocyanate compound (B-2) and by mixing and dispersing them in water.

[0050] As the base resin (B-1) having a functional group crosslinkable with an isocyanate group such as a hydroxyl group etc. in the water-based intermediate paint (B), for example, a polyester resin or an acrylic resin having two or more hydroxyl groups in the molecule is particularly preferred.

[0051] A polyester resin containing hydroxyl group can be prepared by esterifying a polybasic acid and a polyhydric alcohol by a per se known process and has preferably in the range of 1000-50000, particularly 2000-20000 of a number-average molecular weight, 20-200 mgKOH/g, particularly 50- 150 mgKOH/g of a hydroxyl group value and less than 100 mgKOH/g, particularly 10-70 mgKOH/g of an acid value.

[0052] A polybasic acid is a compound having two or more carboxyl groups in the molecule and there can be mentioned, for example, phthalic acid, isophthalic acid, terephthalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, tetrahydrophthalic acid, hexahydrophthalic acid, Het acid[®], maleic acid, fumaric acid, itaconic acid, trimellithic acid, pyromellithic acid, and their anhydrides etc.

[0053] A polyhydric alcohol is a compound having two or more hydroxyl groups in the molecule and there can be mentioned, for example, ethylene glycol, propylene glycol, diethylene glycol, butylene glycol, hexanediol, diethylene glycol, dipropylene glycol, neopentyl glycol, hydrogenated bisphenol A, triethylene glycol, glycerol, trimethylolpropane, pentaerythritol etc.

[0054] An acrylic resin containing hydroxyl group can be prepared by copolymerizing polymerizable monomer components containing a hydroxyl group-containing polymerizable monomer and an acrylic type monomer under the usual condition and has preferably in the range of 1000-50000, particularly 2000-20000 of a number-average molecular weight 20-200 mgKOH/g, particularly 50- 150 mgKOH/g of a hydroxyl group value and less than 100 mgKOH/g, particularly 20-70 mgKOH/g of an acid value.

[0055] A hydroxyl group-containing polymerizable monomer is a compound having one or more of each hydroxyl group and polymerizable unsaturated bond in the molecule and there can be mentioned, for example, monoesterified products of a glycol of carbon number of 2-20 and (meth)acrylic acid such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate etc. and as an acrylic type monomer there can be mentioned monoesterified products of (meth)acrylic acid and a monohydric alcohol of carbon number of 1-22, for example, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, hexyl acrylate, hexyl methacrylate, octyl acrylate, octyl methacrylate, lauryl acrylate, lauryl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate etc.

[0056] In the preparation of an acrylic resin containing hydroxyl group another polymerizable monomer than these polymerizable monomers containing hydroxyl group and acrylic type monomers can be used together.

[0057] As another polymerizable monomer there can be mentioned, for example, C₂-C₁₈ alkoxyalkyl ether of (meth)acrylic acid such as methoxybutyl acrylate, methoxybutyl methacrylate, methoxyethyl acrylate, methoxyethyl methacrylate etc.; amino-(meth)acrylic type monomers such as N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl acrylate, N,N-diethylaminoethyl methacrylate, N-t-butylaminoethyl acrylate, N-t-butylaminoethyl methacrylate, N,N-dimethylaminopropyl acrylate, N,N-dimethylaminopropyl methacrylate etc.; (meth)acrylamide type monomers such as acrylamide, methacrylamide, N-methylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-ethylmethacrylamide, N-butyacrylamide, N-butylmethacrylamide, N-dimethylacrylamide, N-dimethylmethacrylamide etc.; compounds having one or more of each carboxyl group and polymerizable unsaturated bond in the molecule, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid, methaconic acid, their anhydrides and half esterified products etc.; monomers containing glycidyl group such as glycidyl acrylate, glycidyl methacrylate etc.; styrene, α -methylstyrene, vinyltoluene, acrylonitrile, vinyl acetate, vinyl chloride etc.

[0058] Blocked polyisocyanate compound (B-2) is a crosslinking agent for the base resin (B-1) and there can be used specifically one or more substances selected from the substances mentioned as a blocked polyisocyanate compound (A-2) described as a crosslinking agent in the aforementioned cationic electrodeposition paint (A).

[0059] In the water-based intermediate paint (B) the compounding ratio of a base resin (B-1) and a blocked polyisocyanate compound (B-2) is not particularly restricted but preferable in the range of 40-90%, particularly 50-80% of the

base resin (B-1) and 60- 10%, particularly 50-20% of the blocked polyisocyanate compound (B-2) based upon the total solid content weight of said both components.

[0060] The water-based intermediate paint (B) can contain, in addition to a base resin (B-1) and a blocked polyisocyanate compound (B-2), further a curing catalyst in order to accelerate the crosslinking reaction by said both components, extender pigment, color pigment, surface adjustment agent etc. As said curing catalyst there can be used one or more substances selected from the substances mentioned in relation to the above-mentioned cationic electrodeposition paint (A) and its compounding amount is preferred in the range of generally 0.1-10 parts by weight, particularly 0.5-2 parts by weight per 100 parts by weight of the total of the base resin (B-1) and the blocked polyisocyanate compound (B-2).

[0061] In the present invention the starting point of the crosslinking curing of the coating film of the water-based intermediate paint (B) is preferably later compared with the starting point of the crosslinking curing of the coating film of the cationic electrodeposition paint (A) located underneath and specifically its crosslinking curing reaction starts preferably later by 0.5-10 minutes, particularly by 5-10 minutes, than the starting point of the crosslinking curing reaction of the coating film of the cationic electrodeposition paint (A). Namely, the "starting time of curing" required from the start of heating of the coating film of the water-based intermediate paint (B) to the starting point of the crosslinking curing is longer compared with the "starting time of curing" of the coating film of the cationic electrodeposition paint (A) and the difference is suitably between 0.5-10 minutes, particularly 5-10 minutes.

[0062] The starting point of the crosslinking curing of the coating film of water-based intermediate paint (B) can be easily regulated, for example, by suitably selecting the kind, compounding amount etc. of polyisocyanate compound, blocking agent curing catalyst etc. The starting point of the crosslinking curing reaction of the coating film of the water-based intermediate paint (B) is later compared with the starting point of the crosslinking curing reaction of the coating film of the cationic electrodeposition paint (A) and specifically suitable between 5.5-20 minutes, particularly 10-15 minutes, in the coating procedure.

[0063] The water-based intermediate paint (B) can be obtained by mixing and dispersing the base resin (B-1) and the blocked polyisocyanate compound (B-2) and optionally other additives homogeneously in water and the solid content concentration at the coating is preferably regulated in the range of 20-70% by weight.

[0064] In the method of the present invention a cationic electrodeposition paint (A) is coated and, without being cured, after being dried at a temperature below 120°C as necessary, a water-based intermediate paint (B) is coated on the said electrodeposited coating film, and then both coating films are crosslinking cured together by heating.

[0065] The coating of the water-based intermediate paint (B) can be conducted by electrostatic coating, airless spray, air spray etc. and its film thickness is suitably in the range of about 5 -about 80 µm, particularly about 15 - about 35 µm based upon a cured coating film. The heating temperature for the crosslinking curing of both coating films of the cationic electrodeposition paint (A) coating film and the water-based intermediate paint (B) coating film is higher than the dissociation temperature of the blocked polyisocyanate compound contained in said coating films and suitable usually about 130 - about 180°C. The coating films can be cured by baking at the temperature for 10-40 minutes.

[0066] On the multilayered coating film formed by the method of the present invention a topcoat paint such as solid color paint metallic paint and clear paint etc. can be coated as necessary by a known method, for example, 1-coat-1-bake (1C1B), 2-coat-1-bake (2C1B), 2-coat-2-bake (2C2B), 3-coat-1-bake (3C1B) etc.

40 EXAMPLES

[0067] The method of the present invention is hereinafter described more specifically by Examples and Comparative Examples. Parts and % are both by weight.

[0068] The measurement of the starting point of the crosslinking curing of the coating film of cationic electrodeposition paint and coating film of water-based intermediate paint in Examples and Comparative Examples were conducted by using Rigid Body Pendulum Free Damping Oscillation Instrument (Toyo Bordwin Co., Ltd., Leoviblon DDV-OPA Type).

1. Preparation of Samples

1) Polyester resin (1):

[0069] 756 Parts of neopentyl glycol, 109 parts of trimethylolpropane, 370 parts of hexahydrophthalic acid, 292 parts of adipic acid and 398 parts of isophthalic acid were placed in a reaction vessel and, after being reacted at 220°C for 6 hours, 45 parts of trimellitic anhydride was added and reacted at 170°C for 30 minutes to obtain a polyester resin having a number-average molecular weight of about 8000, acid value of 20 mgKOH/g, hydroxyl group value of 95 mgKOH/g.

2) Acrylic resin (1):

[0070] 210 Parts of styrene, 294 parts of n-butyl methacrylate, 253 parts of hydroxybutyl acrylate, 200 parts of 2-ethylhexyl methacrylate, 30 parts of acrylic acid were placed in a reaction vessel and reacted at 120°C for 5 hours to obtain an acrylic resin having a number-average molecular weight of about 20000, acid value of 25 mgKOH/g, hydroxyl group value of 95 mgKOH/g.

3) Cationic electrodeposition paint (1):

[0071] 1260 Parts of bisphenol A type epoxy resin with an epoxy equivalent 630 ("Epiccoat 1002", trade name, made by Shell Chemical Co., Ltd.) was dissolved in 450 parts of butyl cellosolve, to which 132 parts of p-nonylphenol and 105 parts of N-methylethanolamine were added, heated to 140°C and reacted at the temperature to obtain an added epoxy resin with solid content 77%, amine value 52. After adding 30 parts of a blocked polyisocyanate compound (curing agent) and 1.3 parts of polypropylene glycol (number-average molecular weight 4000) to 130 parts of the resin, 2.1 parts of acetic acid was added to water-solubilize, then after adding 6.5 parts of 20% aqueous solution of lead acetate, deionized water was gradually added and dispersed to make an emulsion with 30% solid content.

[0072] On the other hand, after 4.7 parts of 75% epoxy type amine type resin for pigment dispersion had been neutralized with 0.16 parts of 88% aqueous solution of formic acid, 22.2 parts of deionized water was added and further 15 parts of titanium white pigment 7 parts of clay, 0.3 parts of carbon black, 3.0 parts of basic lead silicate and 3 parts of dioctyltin oxide were added and dispersed by a ball mill to make a pigment paste with 55% solid content.

[0073] Then after mixing the above-mentioned emulsion with 30% solid content and this pigment paste with 55% solid content, the mixture was diluted with deionized water to make an electrodeposition bath with 19% solid content.

[0074] The above-mentioned blocked polyisocyanate compound was prepared by reacting 2-ethylhexyl alcohol monoether of ethylene glycol (blocking agent) with the reaction product of 174 parts of 2,6-tolylene diisocyanate and 85 parts of polycaprolactonediol with hydroxyl group equivalent 425.

4) Cationic electrodeposition paint (2):

[0075] It was prepared in the same manner as in the cationic electrodeposition paint (1), except omitting 6.5 parts of 20% aqueous solution of lead acetate in the above-mentioned cationic electrodeposition paint (1) and replacing 3.0 parts of basic lead silicate in the pigment paste with 3.0 parts of bismuth hydroxide.

5) Cationic electrodeposition paint (3):

[0076] It was prepared in the same manner as in the cationic electrodeposition paint (1), except replacing 6.5 parts of 20% aqueous solution of lead acetate in the above-mentioned cationic electrodeposition paint (1) and 3.0 parts of basic lead silicate in the pigment paste with 1 part (as metal bismuth amount) of bismuth dispersion paste.

[0077] The "bismuth dispersion paste" here was prepared as follows.

[0078] 133.3 parts of epoxy type tertiary amine type resin for pigment dispersion (amine value 100) with 75% solid content and 81.1 parts of methoxyacetic acid were compounded in a vessel and after being stirred to a homogeneity, 233.5 parts of deionized water were added drop by drop in the mixture while vigorously stirring and further 111.5 parts of bismuth oxide were added and mixed and dispersed in a ball mill for 20 hours to obtain a bismuth dispersion paste with 50% solid content.

6) Water-based intermediate paint (1):

[0079] 1000 Parts (as solid content amount, same for the followings) of the polyester resin (1), 40 parts of dimethylaminoethanol (*1), 410 parts of aliphatic 6-functional type blocked polyisocyanate compound (*2), 1400 parts of titanium white pigment (*3) and 20 parts of carbon black (*4) were mixed and dispersed in 1800 parts of deionized water to obtain the water-based intermediate paint (1).

(*1) Dimethylaminoethanol: made by Nippon Nyukazai Co., Ltd., trade name: "Aminoalcohol 2Mabs"

(*2) Aliphatic 6-functional type blocked polyisocyanate compound: An adduct of trimer of hexamethylene diisocyanate blocked with methyl ethyl ketoxime.

(*3) Titanium white pigment: "Tayca JR806" (made by Tayca Corporation, trade name)

(*4) Carbon black: "Mitsubishi Carbon Black M- 100" (made by Mitsubishi Chemical Corporation, trade name)

7) Water-based intermediate paint (2):

[0080] 1000 Parts of the polyester resin (1), 40 parts of dimethylaminoethanol (*1), 410 parts of aliphatic 3-functional type blocked polyisocyanate compound (*5), 1400 parts of titanium white pigment (*3) and 20 parts of carbon black (*4) were mixed and dispersed in 1800 parts of deionized water to obtain the water-based intermediate paint (2).

(*5) Aliphatic 3-functional type blocked polyisocyanate compound: Trimer of hexamethylene diisocyanate blocked with methyl ethyl ketoxime.

8) Water-based intermediate paint (3):

[0081] 1000 Parts of the acrylic resin (1), 40 parts of dimethylaminoethanol (*1), 410 parts of aliphatic 3-functional type blocked polyisocyanate compound (*5), 1400 parts of titanium white pigment (*3) and 20 parts of carbon black (*4) were mixed and dispersed in 1800 parts of deionized water to obtain the water-based intermediate paint (3).

9) Water-based intermediate paint (4) (for comparison)

[0082] 1000 Parts of the polyester resin (2), 40 parts of dimethylaminoethanol (*1), 410 parts of aliphatic 3-functional type blocked polyisocyanate compound (*6), 1400 parts of titanium white pigment (*3) and 20 parts of carbon black (*4) were mixed and dispersed in 1800 parts of deionized water to obtain the water-based intermediate paint (4).

(*6) Aliphatic 3-functional type blocked polyisocyanate compound: Trimer of hexamethylene diisocyanate blocked with ethyl malonate.

10) Water-based intermediate paint (5) (for comparison)

[0083] 1000 Parts of the polyester resin (1), 40 parts of dimethylaminoethanol (*1), 300 parts of melamine resin (*7), 1400 parts of titanium white pigment (*3) and 20 parts of carbon black (*4) were mixed and dispersed in 1800 parts of deionized water to obtain the water-based intermediate paint (5).

(*7) Melamine resin: "Cymel 303" (made by Mitsui Cyanamid, Ltd., trade name, methanol-modified melamine resin)

2. Examples 1-5 and Comparative Examples 1-2

[0084] A dull finished steel plate, treated with zinc phosphate, was dipped in an electrodeposition bath of the cationic electrodeposition paints (1)-(3) as cathode, electrodeposited at 30°C, 200V for 3 minutes (the film thickness is 25 μm as cured film), dried at 100°C for 10 minutes, and each of the water-based intermediate paints (1)-(5) was coated by air spray (the film thickness is 30-35 μm as cured film), and then heated at 170°C for 30 minutes to cure both coating films through crosslinking.

[0085] The performance test of the multilayered coating film thus obtained was conducted. Test results are shown in Table 1.

Table 1

	Examples				Comparative Examples		
	1	2	3	4	5	1	2
Cationic electrodeposition paint Starting time of crosslinking curing: minutes	(1) 10	(1) 10	(1) 10	(2) 10	(3) 10	(1) 10	(1) 10
Intermediate paint Starting time of crosslinking curing: minutes	(1) 12	(2) 13	(3) 11	(1) 12	(1) 12	(4) 8	(5) 9
Gloss	92	95	90	92	93	63	68
Image sharpness	82	86	81	82	84	48	52
Chipping resistance	○	○	○	○	○	△	X

Table 1 (continued)

		Examples				Comparative Examples		
		1	2	3	4	5	1	2
5	Impact resistance	50<	50<	50<	50<	50<	40	30
	Moisture resistance	Appearance	○	○	○	○	○	○
		Adhesivity	○	○	○	○	○	○

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[0086] Test methods are as follows.

Gloss: 60° Specular reflectivity

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Image sharpness: Results measured by Image Clarity Meter (made by SUGA TEST INSTRUMENT CO., LTD). Figures in the table are ICM values and in the range of 0-100. The bigger the figure is, the better is the image sharpness. ICM value of over 80 shows a very good image sharpness.

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Chipping resistance: Using "Q-G-R Gravelometer" (made by Q Panel Co., Ltd.) 100g of crushed stones of 15-20 mm diameter were blown onto the coating surface at an angle of 90° at -20°C by an air pressure of about 4 kg/cm². After that the condition of the coating surface was visually evaluated. ○ shows that a little impact scratch is observed on the intermediate coating surface, but there is no peeling of the electrodeposited coating film at all. △ shows that relatively many impact scratches are observed on the intermediate coating surface and there is a little peeling of the electrodeposited coating film, too. X shows that many impact scratches are observed on the intermediate coating surface and there are considerable amount of peeling of the electrodeposited coating film.

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Impact resistance: Using a DuPont impact test machine a falling weight of 500 g with a diameter of impact point of 1/2 inches was let fall on the coating surface placed upside and the falling distance (height cm), at which no crack be formed on the coating film, was measured.

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Moisture resistance: After the test plate had been left for 72 hours under the condition of 50°C, 95% humidity, the appearance and adhesivity of the coating film were examined. Evaluation of the appearance: ○ shows that no abnormality at all; △ shows that a little blistering and/or chipping is observed; X shows that much blistering and/or chipping are observed. Adhesivity test was conducted by squares (100 squares of 1mm x 1mm size) tape peeling test and when 90 or more squares of coating film left unpeeled, it is classified as ○.

Claims

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1. A method of forming a multilayered coating film by coating a cationic electrodeposition paint, containing a blocked polyisocyanate compound as a crosslinking agent, forming an intermediate coating film by coating a water-based intermediate paint containing a blocked polyisocyanate compound as a crosslinking agent on the formed, electrodeposited coating film without curing said electrodeposited coating film, and then heating both coating films to form a multilayered coating film by curing both together, characterized by regulating so that the crosslinking curing reaction of said electrodeposited coating film starts earlier than the crosslinking curing reaction of said intermediate coating film.

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2. The method of forming a multilayered coating film set forth in Claim 1 wherein the curing temperature of the coating film of the cationic electrodeposition paint is set lower than the curing temperature of the coating film of the intermediate paint.

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3. The method of forming a multilayered coating film set forth in Claim 1 wherein the temperature difference between the curing temperature of the coating film of the cationic electrodeposition paint and the curing temperature of the coating film of the intermediate paint is in the range of 5-20°C.

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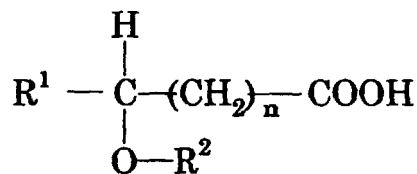
4. The method of forming a multilayered coating film set forth in Claim 1 wherein the temperature difference between the curing temperature of the coating film of the cationic electrodeposition paint and the curing temperature of the coating film of the intermediate paint is in the range of 5-15°C.

5. The method of forming a multilayered coating film set forth in Claim 1 wherein the starting time of curing of the coating film of the cationic electrodeposition paint is between 5-15 minutes.

6. The method of forming a multilayered coating film set forth in Claim 1 wherein the cationic electrodeposition paint

is a lead-free cationic electrodeposition paint comprising further a bismuth-containing compound.

- 5 7. The method of forming a multilayered coating film set forth in Claim 6 wherein the bismuth-containing compound is selected from bismuth hydroxide, bismuth trioxide, bismuth nitrate, bismuth benzoate, bismuth citrate, bismuth oxy-carbonate and bismuth silicate.
- 10 8. The method of forming a multilayered coating film set forth in Claim 6 wherein the bismuth-containing compound is a water dispersion paste, obtained by mixing and dispersing a water-insoluble bismuth compound and an aliphatic carboxylic acid represented by the following general formula



20 wherein R¹ represents a hydrogen atom or an alkyl group of 1-3 carbon atoms; R² represents a hydrogen atom or an alkyl group of 1-10 carbon atoms; n is 0 or 1,

25 in an aqueous medium in the presence of a dispersant, in which an aliphatic carboxylic acid-modified bismuth compound exists in a non-water-soluble state.

- 30 9. A method of forming a multilayered coating film wherein the difference between the starting time of curing of the coating film of the cationic electrodeposition paint and the starting time of curing of the coating film of the intermediate paint is 0.5-10 minutes.
10. The method of forming a multilayered coating film set forth in Claim 1 wherein the heat curing is conducted at a temperature of about 130 - about 180°C.
- 35 11. The method of forming a multilayered coating film set forth in Claim 1 wherein a topcoat paint is further coated on the coating film of the intermediate paint.
12. An article on which a multilayered coating film is formed by the method set forth in Claim 1.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/04099

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ B05D1/36, B05D7/24		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ B05D1/36, B05D7/24		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Toroku Koho 1996-1998		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 6-228796, A (Herberts GmbH.), 16 August, 1994 (16. 08. 94)	1-5, 9-12
Y	& US, 5389406, A & EP, 595186, A & CA, 2108744, A	6-8
Y	JP, 7-163936, A (Herberts GmbH.), 27 June, 1995 (27. 06. 95) & US, 5507928, A & EP, 646420, A & CA, 2132174, A	6-8
A	JP, 60-251973, A (Nippon Paint Co., Ltd.), 12 December, 1985 (12. 12. 85) (Family: none)	1-12
A	JP, 64-73099, A (Nissan Motor Co., Ltd.), 17 March, 1989 (17. 03. 89) (Family: none)	1-12
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 7 December, 1998 (07. 12. 98)		Date of mailing of the international search report 15 December, 1998 (15. 12. 98)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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