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(54) Title: WATER-BORNE CLEAR COATING COMPOSITION AND METHOD OF FORMING CLEAR COATING FILM

(57) Abstract: It is an object of the present invention to provide a water-borne clear coating composition and a method of forming a clear coating film, which can control a sagging suitably and form a coating film having a good appearance and in which consideration is given to environments. A water-borne clear coating composition, containing an active energy-ray curable compound having an unsaturated bond, a photopolymerization initiator, a water-borne acrylic resin and a melamine resin.

DESCRIPTION

WATER-BORNE CLEAR COATING COMPOSITION AND METHOD OF FORMING CLEAR COATING FILM

TECHNICAL FIELD

The present invention relates to a water-borne clear coating composition and a method of forming a clear coating film.

BACKGROUND ART

In coating of automotive bodies, the formation of a top coating film consisting of a base coating film and a clear coating film is in widespread use. Particularly, since the clear coating film constitutes the outermost layer in a coating film of automotive bodies and the like, properties such as high appearance, water resistance and weather resistance are required, and as a clear coating composition having such properties, various clear coating compositions are used.

On the other hand, in the field of automotive coatings, an effort is under way to reduce amounts of organic solvents to be used from the viewpoint of consideration to environments. In order to achieve such an object, it is studied to convert a solvent-borne coating composition to a water-borne coating composition, and in an intermediate coating composition and a base coating composition, this conversion has already become commercially practical. But, in a clear coating composition, this conversion has been delayed since it was difficult to satisfy all of required properties described above.

Particularly, in the water-borne clear coating composition, it is desired to control adequately a sagging. Since the occurrence of the sagging causes projections and depressions at the surface of a coating film and thereby the smoothness of a coating film is deteriorated and a defective appearance is produced, it is a very important issue that to prevent the sagging from taking place. Particularly, it was

extremely difficult to control the smoothness of a coating film since an automotive body has a complicated structure. Such a problem arises also in a solvent-borne clear coating composition, but the deterioration of an appearance due to such a problem is relatively slight in the solvent-borne clear coating composition since the viscosity of a coating composition is increased due to volatilization of a solvent in the solvent-borne clear coating composition. However, in the water-borne clear coating composition, since vaporization of water is slow, such a problem becomes more significant.

For example, as for a close-to-horizontal plane of a substrate to be coated, it is not preferred to coat the surface with a coating composition having excessively high viscosity in order to attain the smoothness of the surface. When a coating film is formed from a coating composition having low viscosity, a smooth surface is formed spontaneously, and contrarily, when the coating film is formed from a coating composition of high viscosity, the coating composition is not fluidized and therefore the surface is less prone to being leveled.

On the other hand, on a close-to-vertical plane, a coating composition of low viscosity readily run down, and therefore the coating film requires a measure of viscosity. However, since it is not practical to switch the kinds of a coating composition to be used between the close-to-horizontal plane and the close-to-vertical plane, it is required to achieve the smoothness on the above-mentioned horizontal plane and the smoothness on the above-mentioned vertical plane simultaneously with the same coating composition.

In Japanese Kokai Publication Hei11-300272, there is described a method of forming a coating film, comprising the steps of applying a melamine-based coating composition containing a active energy-ray curable compound to a substrate to be coated, irradiating active energy-rays to pre-curing a coating film, and heating to cure a coating film completely in order to control sagging in an intermediate coating composition.

In Japanese Kokai Publication 2003-245606, there is described a method of forming a heat cured coating film, comprising the steps of applying a coating composition containing a photo-curable composition, a thermosetting resin composition, a photopolymerization initiator, and a photoacid generator, irradiating light to the coating film to increase the viscosity of the coating film, and heating and curing the coating film. However, these methods are a method of forming a coating film by curing a coating composition containing an organic solvent and a method of coating a water-borne clear coating composition, in which a problem of deteriorating an appearance due to sagging is remarkable, is not described. Further, when the photoacid generator is used, there is a possibility that properties such as the water resistance and the weather resistance of a coating film are deteriorated, and therefore it has been required to form a coating film having higher water resistance and higher weather resistance.

DISCLOSURE OF THE INVENTION

In view of the above state of the art, it is an object of the present invention to provide a water-borne clear coating composition and a method of forming a clear coating film, which can control a sagging suitably and form a coating film having a good appearance and in which consideration is given to environments.

The present invention pertains to a water-borne clear coating composition,

containing an active energy-ray curable compound having an unsaturated bond, a photopolymerization initiator, a water-borne acrylic resin and a melamine resin.

The active energy-ray curable compound having an unsaturated bond is preferably a compound having a (meth)acrylate group.

The present invention pertains to a method of forming a clear coating film,

comprising steps of applying the water-borne clear coating composition mentioned above to a substrate to be coated (step 1),

irradiating active energy-rays to a not-yet-cured coating film obtained by the step 1 from an approximately vertical plane (step 2), and

heating the substrate to be coated, which has been subjected to the step 2, to give a cured coating film (step 3).

The viscosity of the coating film which has been subjected to the step 2 is preferably 2000 to 500000 mPa•s.

In the method of forming a clear coating film of the present invention, said method preferably comprises the step (A-1) of applying an intermediate coating composition onto a cured electrodeposition coating film and heat curing the intermediate coating composition applied to form a multilayer coating film, and the step (A-2) of applying a base coating composition onto said multilayer coating film, prior to the step 1.

In the method of forming a clear coating film of the present invention, said method preferably comprises the step (B-1) of applying an intermediate coating composition onto a not-yet-cured electrodeposition coating film and heat curing the intermediate coating composition applied and the not-yet-cured electrodeposition coating film to form a multilayer coating film, and the step (B-2) of applying a base coating composition onto said multilayer coating film, prior to the step 1.

In the method of forming a clear coating film of the present invention, said method preferably comprises a step (C) of applying a overcoat clear coating composition to the substrate after the step 3.

The present invention pertains to a coated substrate,

wherein a substrate to be coated is an automotive body or an automotive assembly part and said coated substrate is coated by the method mentioned above.

Hereinafter, the present invention will be described in

detail.

The water-borne clear coating composition and the method of forming a clear coating film of the present invention is characterized by using an active energy-ray curable compound having an unsaturated bond and a photopolymerization initiator in combination with a water-soluble thermosetting resin component. When active energy-rays are irradiated after applying a coating composition containing the above-mentioned active energy-ray curable compound having an unsaturated bond and the above-mentioned photopolymerization initiator to a substrate to be coated, a polymerization reaction of the above active energy-ray curable compound having an unsaturated bond takes place due to the irradiation of the active energy-ray and an increase in the viscosity of the coating film takes place. When the increase in the viscosity of the coating film takes place, sagging becomes hard to occur and an appearance of a clear coating film can be controlled.

By employing such a coating composition and applying the above-mentioned method, an excellent effect of inhibiting sagging can be attained even in the case of a water-borne clear coating composition and an environmental load of the clear coating composition can be reduced.

The present invention pertains to the water-borne clear coating composition contains an active energy-ray curable compound having an unsaturated bond, a photopolymerization initiator, a water-borne acrylic resin and a melamine resin. The above-mentioned active energy-ray curable compound having an unsaturated bond is preferably a compound having two or more α,β-unsaturated carbonyl groups in a molecule. The above-mentioned α,β-unsaturated carbonyl group is a functional group in which a double bond exists between α carbon and β carbon on a carbonyl group and examples of the functional groups can include a methacrylate group, an acrylate group, a maleate group and a fumarate group. When the above active energy-ray curable compound has only one α,β-unsaturated carbonyl group, it is not

preferred in that active energy-ray curability is not adequately exhibited. Number of the above α,β-unsaturated carbonyl groups in a molecule is preferably 10 or less and most preferably 6 or less.

The above active energy-ray curable compound having an unsaturated bond is not particularly limited, and it can include, for example, polyol (meth)acrylate ester, unsaturated polyester polymer containing α,β-unsaturated dicarboxylic acid such as fumaric acid and maleic acid as an acid component, epoxy polymer (meth)acrylate, a (meth)acryloyl group-containing urethane compound, an acrylic polymer containing an α,β-unsaturated carbonyl group, a (meth)acryloyl group-containing polyether polymer and a (meth)acryloyl group-containing silicone oligomer.

The above-mentioned polyol (meth)acrylate ester is ester of polyol having two or more hydroxyl groups and acrylic acid. The above-mentioned compound having two or more hydroxyl groups may be a low molecular weight compound or may be a polymer. The above polyol (meth)acrylate ester is not particularly limited, and it can include, for example, (meth)acrylate esters of low molecular weight polyol such as ethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerithritol tetra(meth)acrylate, dipentaerithritol hexa(meth)acrylate, 1,4-cyclohexyldimethanol di(meth)acrylate, 4,4'-isopropylidenedicyclohexanol di(meth)acrylate, bis(hydroxymethyl)tricyclo[5,2,1,0]decane di(meth)acrylate and 1,3,5-tris(2-hydroxyethyl)cyanurate tri(meth)acrylate; and (meth)acrylate esters of a hydroxyl group-containing polymer such as (meth)acrylate of an acrylic polymer having a hydroxyl group, (meth)acrylate of polyester polyol, (meth)acrylate of polyether polyol, (meth)acrylate of epoxy polyol, (meth)acrylate of polyurethane polyol and poly(meth)acrylate of silicone polyol. In the present specification, (meth)acrylate refers to acrylate and methacrylate.

The above-mentioned unsaturated polyester polymer is not particularly limited, and it can include, for example, polymer obtained by polycondensation of an acid component consisting of α,β-unsaturated dicarboxylic acid such as maleic acid anhydride and fumaric acid and another polyhydric carboxylic acid used as required, and polyol having two or more hydroxyl groups.

Polyol used for the above unsaturated polyester polymer is not particularly limited, and it can include, for example, ethylene glycol, diethylene glycol, propylene glycol, tetramethylene glycol, 1,6-hexanediol, neopentyl glycol, trimethylolpropane, glycerin, pentaerythritol, 1,4-cyclohexanedimethanol, 4,4'-isopropylidenedicyclohexanol, bis(hydroxymethyl)tricyclo[5,2,1,0]decane, 1,3,5-tris(2-hydroxyethyl)cyanuric acid, isopropylidenebis(3,4-cyclohexanediol), and ethylene oxide adduct, propylene oxide adduct and/or caprolactone adduct thereof.

Another polyhydric carboxylic acid, which can be used for the above unsaturated polyester polymer, is not particularly limited, and it can include, for example, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, methyltetrahydrophthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, itaconic acid, adipic acid, azelaic acid, sebacic acid, succinic acid, dodecenylsuccinic acid and 1,4-cyclohexanedicarboxylic acid.

The above-mentioned epoxy polymer (meth)acrylate can include, for example, a polymer obtained by a ring-opening addition reaction of an epoxy polymer such as a bisphenol type epoxy polymer and a novolak type epoxy polymer and (meth)acrylic acid.

The above-mentioned (meth)acryloyl group-containing urethane compound can include, for example, a compound obtained by an addition reaction of a polyisocyanate compound such as

isophorone diisocyanate, trilene diisocyanate, diphenylmethane diisocyanate and hexamethylene diisocyanate or urethane prepolymer thereof, and 2-hydroxyethyl (meth)acrylate.

The above-mentioned acrylic polymer containing an α,β-unsaturated carbonyl group can include, for example, an acrylic polymer having a (meth)acrylate group on a side chain, which is obtained by reacting an acrylic polymer formed by copolymerizing glycidyl (meth)acrylate with (meth)acrylic acid; and an acrylic polymer having a (meth)acrylate group on a side chain, which is obtained by reacting a carboxyl group-containing acrylic polymer with an epoxy group-containing acrylic monomer such as glycidyl (meth)acrylate.

The above-mentioned (meth)acryloyl group-containing polyether polymer can include, for example, a compound obtained by reacting polyether having a hydroxyl group at a terminal with 2-(meth)acryloyloxyethyl isocyanate.

The above-mentioned (meth)acryloyl group-containing silicone oligomer can include, for example, polyorganosiloxane having 3-(meth)acryloyloxypropyl groups at both terminals.

The above active energy-ray curable compound having an unsaturated bond may have a plurality of hydroxyl groups and the like in addition to the α,β-unsaturated carbonyl group. The above-mentioned active energy-ray curable compounds having an unsaturated bond may be used alone or in combination of two or more kinds.

The active energy-ray curable compound having an unsaturated bond contained in the coating composition of the present invention is preferably polyol (meth)acrylate ester because polyol (meth)acrylate ester is highly reactive and has excellent weather resistance and compatibility and a high gloss.

A number-average molecular weight (Mn) of the active energy-ray curable compound having an unsaturated bond contained in the coating composition of the present invention is preferably within a range of 200 (lower limit) to 5000 (upper limit). When the above-mentioned number-average molecular weight (Mn) is less

than 200, the solvent resistance, the water resistance and the weather resistance of a coating film may be deteriorated due to vaporization during heat curing, reduction in the hardness of a coating film and reduction in the curability of a coating film. When the above number-average molecular weight (Mn) is more than 5000, the viscosity of the active energy-ray curable compound having an unsaturated bond itself increases and a content of a solution in a diluted coating composition upon applying a coating composition may become large in some cases. The above lower limit is more preferably 250. The above upper limit is more preferably 3000. In addition, the number-average molecular weight (Mn) is a number-average molecular weight on the polystyrene equivalent basis measured by GPC (gel permeation chromatography) in the present specification.

A double bond equivalent of the above-mentioned active energy-ray curable compound having an unsaturated bond is preferably within a range of 50 (lower limit) to 1500 (upper limit). When the above double bond equivalent is less than 50, an unreacted (meth)acrylate group remains in a coating film to be obtained and therefore the weather resistance of a coating film may be deteriorated or a coating film to be obtained may become hard and brittle. And, when the above double bond equivalent is more than 1500, a crosslinking density of a coating film to be obtained becomes low and therefore coating film properties and performance may be deteriorated. In addition, the double bond equivalent in the present specification means a molecular weight per a double bond. The above double bond equivalent more preferably has a lower limit of 70 and an upper limit of 1000.

A commercially available article of the above active energy-ray curable compound having an unsaturated bond can include A-TMM-3L (trade name, produce by SHIN-NAKAMURA CHEMICAL Co., Ltd.), M-400 (trade name, produced by TOAGOSEI Co., Ltd.), TMPTA: (trade name, produced by TOAGOSEI Co., Ltd.), and D-330: (trade name, produced by Nippon Kayaku Co., Ltd.).

The content of the above active energy-ray curable compound having an unsaturated bond is preferably 1 weight % (lower limit) to 35 weight % (upper limit) in 100 weight % of the total resin solid matter of the water-borne acrylic resin and the melamine resin. When this content is less than 1 weight %, an effect may not be developed. When the content is more than 35 weight %, this may have an adverse effect on coating film properties. The above content more preferably has a lower limit of 5 weight % and an upper limit of 30 weight %.

The water-borne clear coating composition of the present invention further has a photopolymerization initiator.

As the above-mentioned photopolymerization initiator, a publicly known initiator can be employed, and specific examples of the initiators can include benzoin and benzoin alkyl ethers such as benzoin, benzoin methyl ether, benzoin ethyl ether and benzoin propyl ether; acetophenones such as acetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone and 1,1-dichloroacetophenone; aminoacetophenones such as 2-methyl1-[4-(methylthio)phenyl]-2-morpholinopropanone-1,2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 and N,N-dimethylaminoacetophenone; anthraquinones such as 2-methylanthraquinone, 2-ethylanthraquinone, 2-tert-butylanthraquinone and 1-chloroanthraquinone; thioxanthones such as 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2-chlorothioxanthone and 2,4-diisopropylthioxanthone; ketals such as acetophenonedimethylketal and benzyldimethylketal; benzophenones or xanthones such as benzophenone and 4,4'-bisdiethylaminobenzophenone; and 2,4,6-trimethylbenzoyldiphenylphosphine oxide. These may be used in combination of two or more kinds and may be further used in combination with tertiary amine such as triethanolamine or a photopolymerization initiator such as ethyl dimethylaminobenzoate.

A commercially available article of the above photopolymerization initiator can include Darocur 1173, Irgacure 184, Irgacure 500, Irgacure 2959 (trade name, every produced by Ciba Specialty Chemicals K.K.).

An amount of the above photopolymerization initiator to be mixed is not particularly limited and it is appropriately established in accordance with a ratio of a heat curing reaction and a photocuring reaction. Further, the amount of the above photopolymerization initiator to be mixed can be adjusted in accordance with a degree of weather resistance required, kinds and amounts of additives such as an ultraviolet absorber component. An amount of the above photopolymerization initiator to be generally mixed in a coating composition containing a curable binder used in the present invention is, for example, 0.01 to 10 weight % with respect to 100 weight % of the above active energy-ray curable compound having an unsaturated bond.

The water-borne clear coating composition of the present invention further contains the water-borne acrylic resin. Since an acrylic resin is highly resistant to hydrolysis, by using this resin, the coating composition of the present invention becomes a water-borne clear coating composition which can attain a coating composition which is excellent in long-term storage stability.

The above-mentioned water-borne acrylic resin is a copolymer which is predominantly composed of acrylic acid and/or methacrylic acid, and a monomer used for polymerizing the above water-borne acrylic resin is not particularly limited and can include, for example, ethylenic unsaturated carboxylic acid monomers such as acrylic acid, methacrylic acid, maleic acid, itaconic acid and the like; ethylenic unsaturated carboxylic alkyl ester monomers such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and the like; ethylenic unsaturated dicarboxylic monoester monomers such as ethyl maleate, butyl maleate, ethyl

itaconate, butyl itaconate and the like; hydroxyl group-containing ethylenic unsaturated carboxylic alkyl ester monomers such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, a reactant of 2-hydroxyethyl (meth)acrylate and ε-caprolactone and the like; ethylenic unsaturated carboxylic aminoalkyl ester monomers such as aminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, butylaminoethyl (meth)acrylate and the like; ethylenic unsaturated carboxylic acid aminoalkylamide monomers such as aminoethyl(meth)acrylamide, dimethylaminomethyl(meth)acrylamide, methylaminopropyl(meth)acrylamide and the like; another amide group-containing ethylenic unsaturated carboxylic acid monomers such as acrylamide, methacrylamide, N-methylolacrylamide, methoxybutylacrylamide, diacetoneacrylamide and the like; unsaturated fatty acid glycidyl ester monomers such as glycidyl acrylate, glycidyl methacrylate and the like; vinyl cyanide monomers such as (meth)acrylonitrile, α-chloroacrylonitrile and the like; saturated aliphatic carboxylic acid vinyl ester monomers such as vinyl acetate, vinyl propionate and the like; styrenic monomers such as styrene, α-methyl styrene, vinyl toluene and the like. A mixture of the above monomers may be in the form of using the above monomers alone or in combination of two or more components.

A polymerization method for obtaining the above acrylic resin is not particularly limited and publicly known methods such as solution polymerization, dispersion polymerization and emulsion polymerization can be employed.

The above acrylic resin may be one obtained by further grafting an acrylic resin obtained from the mixture of the above monomers. By grafting the above acrylic resin, it is possible to change a structure of the acrylic resin for a structure which is further resistant to hydrolysis. And, when the above acrylic resin is grafted, the viscosity of a coating composition resists

increasing even when the acrylic resin is contained in high concentrations in the water-borne coating composition, and therefore it is possible to coat at a high solid content and improve coating efficiency.

A method of grafting described above is not particularly limited and publicly known methods such as solution polymerization, emulsion polymerization and the like can be employed.

A number-average molecular weight of the water-borne acrylic resin of the present invention is preferably within a range of 1000 (lower limit) to 10000 (upper limit). When the above-mentioned number-average molecular weight of an acrylic resin is less than 1000, a molecular weight is too low and therefore the weather resistance and the curability as a clear coating film are low, and basic properties as a clear coating film may be impaired. And, when the number-average molecular weight is more than 8000, since the viscosity of the clear coating composition becomes too large, a dilution ratio of the clear coating composition is increased and coated components become less, and therefore the range of a coating method may be narrowed. The above lower limit is more preferably 1500 and furthermore preferably 2000. The above upper limit is more preferably 7500 and furthermore preferably 6000.

In the above-mentioned water-borne acrylic resin, a hydroxyl group value of resin is more preferably within a range of 30 mg KOH/g (lower limit) to 150 mg KOH/g (upper limit). When the hydroxyl group value is less than 30 mg KOH/g, a crosslinking property becomes insufficient and there may be cases where adequate coating film performance cannot be secured. When it is more than 150 mg KOH/g, the water resistance and the weather resistance of a coating film of a coating composition obtained by using this resin may be deteriorated. The above hydroxyl group value more preferably has a lower limit of 40 mg KOH/g and furthermore preferably has a lower limit of 50 mg KOH/g. The above hydroxyl group value more preferably has an upper limit

of 130 mg KOH/g and furthermore preferably has an upper limit of 100 mg KOH/g.

In the above-mentioned water-borne acrylic resin, an acid value of resin is preferably within a range of 10 mg KOH/g (lower limit) to 100 mg KOH/g (upper limit). When the acid value is less than 10 mg KOH/g, water solubility may be deteriorated to impair stability. When it is more than 100 mg KOH/g, a hydrophilic property of a resin may become too large and therefore water resistance and weather resistance of a coating film may be deteriorated. The above acid value more preferably has a lower limit of 20 mg KOH/g and furthermore preferably has a lower limit of 30 mg KOH/g. The above acid value more preferably has an upper limit of 80 mg KOH/g and furthermore preferably has an upper limit of 60 mg KOH/g.

The above water-borne acrylic resin is preferably contained in an amount 50 weight % (lower limit) to 95 weight % (upper limit) with respect to the total resin solid matter contained in the water-borne clear coating composition. When this amount is less than 50 weight %, it may become difficult to secure the water resistance, the weather resistance and the appearance of a coating film to be obtained. When this amount is more than 95 weight %, a crosslinking property becomes insufficient and there may be cases where adequate coating film performance cannot be secured. The above lower limit is more preferably 65 weight % and the above upper limit is more preferably 90 weight %.

The water-borne clear coating composition of the present invention further contains the above-mentioned melamine resin. The above melamine resin is not particularly limited, and a melamine resin normally used as a curing agent can be used. Among others, a hydrophobic melamine resin is preferred. The reason for this is that an appearance of a coating film to be obtained is improved.

As the above-mentioned hydrophobic melamine resin, for example, an alkyl-etherified melamine resin which is

alkyl-etherified is preferred, and a melamine resin having a methoxy substituent and/or a butoxy substituent is more preferred. Such melamine resins can include CYMEL 325, CYMEL 327, CYMEL 370 and MYCOAT 723 (everything is a trade name, produced by Mitsui Cytec, Ltd.) as a melamine resin having a methoxy group alone; CYMEL 202, CYMEL 204, CYMEL 232, CYMEL 235, CYMEL 236, CYMEL 238, CYMEL 254, CYMEL 266 and CYMEL 267 (everything is a trade name, produced by Mitsui Cytec, Ltd.) as a melamine resin having both of a methoxy group and a butoxy group; and MYCOAT 506 (trade name, produced by Mitsui Cytec, Ltd.), UVAN 20N-60 and UVAN 20SE (everything is a trade name, produced by Mitsui Chemicals Co., Ltd.) as a melamine resin having a butoxy group alone. These may be used alone or in combination of two or more kinds. Among others, CYMEL 327 and MYCOAT 723 are preferred in that the obtained appearances are good by virtue of the compatibility with and the reactivity with the water-borne acrylic resin.

An amount of the above melamine resin to be added is preferably 5 weight % (lower limit) to 50 weight % (upper limit) with respect to 100 weight % of the resin solid matter of the above water-borne clear coating composition. When this amount is less than 5 weight %, a crosslinking property becomes insufficient and there may be cases where adequate coating film performance cannot be obtained. When this amount is more than 50 weight %, there may be cases where the appearance, the water resistance and the weather resistance of a coating film to be obtained cannot be secured. The above lower limit is more preferably 10 weight % and the above upper limit is more preferably 35 weight %.

In the above water-borne clear coating composition, an ultraviolet absorber, a hindered amine light stabilizer, an antioxidant, a crosslinking resin particle, and a surface control agent in addition to the above polymers may be mixed. When the above-mentioned crosslinking resin particle is used, the crosslinking resin particle is preferably mixed in an amount 0.01 weight % (lower limit) to 10 weight % (upper limit) with

respect to the resin solid matter of the water-borne clear coating composition of the present invention. The above lower limit is more preferably 0.1 weight % and the above upper limit is more preferably 5 weight %. When an amount of the above crosslinking resin particle to be added is more than 10 weight %, an appearance of a coating film to be obtained is deteriorated, and when it is less than 0.01 weight %, an effect of controlling rheology cannot be attained.

A method of producing the above water-borne clear coating composition is not particularly limited and methods, which are well known to those skilled in the art, such as a method of kneading and dispersing a formulation of the above polymers and the like with a kneader or a roller, and the like can be employed.

The coating composition of the present invention is water-borne, and it does not need to take the volatilization portion of a solvent into consideration in adjusting viscosity, can control sagging suitably and can reduce the environmental loads. A solution used in the above water-borne coating composition is not particularly limited, and it can include, for example, well known solutions such as Byketol-Special, Byketol-OK (trade names, both produced by BYK-Chemie Japan KK) and the like. In the water-borne clear coating composition, it is preferred to adjust the viscosity in applying the coating composition so as to be 20 to 50 seconds at 20°C with a Ford cup No. 4. By limiting the viscosity of a coating composition within this range, a coating film after coating has excellent smoothness and sagging can be suitably prevented.

The present invention also pertains to a method of forming a clear coating film, which is constituted by using the water-borne clear coating composition described above. The method of forming a clear coating film of the present invention comprises steps of applying the water-borne clear coating composition described above to a substrate to be coated (step 1), irradiating active energy-rays to a not-yet-cured coating film obtained by the step 1 from an approximately vertical plane

(step 2), and heating the coated substrate, which has been subjected to the step 2, to cure the not-yet-cured coating film (step 3).

The method of forming a clear coating film of the present invention is a method in which a coating film can be formed without causing sagging even though a coated plane is approximately vertical by employing the water-borne clear coating composition described above and coating by the coating steps described above.

The above-mentioned step 1 is a step of applying the water-borne clear coating composition described above to a substrate to be coated. In the above step 1, a method of applying a coating composition containing a curable binder is not particularly limited, and it can include, for example, brush application, roller application, air spray application, airless spray application, immersion application, flow coating and the like. Particularly, when the substrate to be coated is an automotive body or an automotive part, electrostatic air spray coating or rotary atomization type electrostatic coating is preferred. The viscosity of the above-mentioned coating composition containing a curable binder can be appropriately adjusted with water in accordance with a coating method. A film thickness of a coating composition applied is not particularly limited and it can be appropriately established in accordance with the applications of a coated substrate to be obtained.

A method of coating the above clear coating composition can include, specifically, a method of coating by an electrostatic coating apparatus of rotary atomization type, referred to as a MicroMicrobell, or a Microbell. A film thickness of the above clear coating composition applied in the above step 1 is preferably within a range of 25 μm (lower limit) to 45 μm (upper limit) in terms of a dried film thickness.

The above-mentioned step 2 is a step of irradiating active energy-rays to a not-yet-cured coating film obtained by the above step 1 from an approximately vertical plane. That is, in the step 2, by irradiating active energy-rays to approximately

vertical plane on which sagging is particularly apt to occur, the viscosity of the coating composition is increased to inhibit sagging, and thereby the smoothness of a coating film is improved and a surface appearance of a coating film becomes better.

The above step 2 is a step in which since the active energy-rays are irradiated from an approximately vertical plane, sagging on a vertical plane or a close-to-vertical place, on which sagging is particularly apt to occur, is inhibited and thereby projections and depressions at the surface of a coating film are inhibited and the surface appearance of a coating film is improved. Herein, the irradiation of the active energy-rays from an approximately vertical plane refers to irradiating from a plane approximately perpendicular to a horizontal plane, but the direction of irradiation have not to be precisely perpendicular and it means that the active energy-rays are irradiated at such an angle that a sufficient amount of active energy-rays can be irradiated to a vertical plane or a close-to-vertical plane on which sagging is apt to occur. In the above step 2, the active energy-rays are irradiated at least from the approximately vertical plane, but it may be simultaneously irradiated from a horizontal plane.

The irradiation of the active energy-ray in the above step 2 can include irradiation of active energy-rays such as ultraviolet light, sun light, visible light, a microwave and an electron beam, but among others, the irradiation of the active energy-ray is particularly preferably performed by the irradiation of ultraviolet light. The above-mentioned irradiation of ultraviolet light can be performed by irradiating using a carbon arc lamp, an electrodeless lamp, a mercury-vapor lamp, a xenon lamp, a fluorescent lamp and argon glow discharge as an ultraviolet source. Among others, the electrodeless lamp is preferred because it can irradiate light uniformly to a substrate to be coated, which has a complicated structure.

The above step 2 may be performed just after the step 1, or a preheating step is performed after the step 1 and the above

step 2 may be performed after the preheating step, but the above step 2 is preferably performed just after the step 1. The irradiation intensity of ultraviolet light in the step 2 is preferably 200 to 2000 mJ/cm^2 and the irradiation time is preferably several seconds.

After subjecting the coating film to the step 2, it is preferred to adjust the composition of a water-borne clear coating composition and the conditions of irradiating the active energy-rays in such a way that the viscosity of the coating film is 2000 to 500000 mPa•s. When the viscosity of a coating film is less than 2000 mPa•s, there is a possibility that sagging cannot be adequately inhibited. When it is more than 500000 mPa•s, this may cause a problem that smoothness of a coating film is lost and a defective appearance such as an orange peel and the like is produced. The viscosity of a coating film more preferably has a lower limit of 5000 mPa•s and an upper limit of 100000 mPa•s.

The above-mentioned step 3 is a step of heating a coated substrate, which has been subjected to the step 2, to cure a coating film. The conditions of the above step 3 varies with the composition of a coating composition to be used, and they can be appropriately established by those skilled in the art, but a heating temperature is generally 80 to 200°C, preferably 100 to 180°C and a heating time is preferably 10 to 40 minutes.

The method of forming a clear coating film of the present invention may have a step (step 4) of further irradiating active energy-rays to a coating film which has been subjected to the above step 3. If an active energy-ray curable compound having an unsaturated bond, which has not reacted in the above step 2, remains, there is a possibility that properties of a coating film such as weather resistance may be deteriorated, and if the above step 4 is carried out, this possibility can be eliminated. The above-mentioned step 4 is a step by which a carbon-carbon unsaturated double bond in the above active energy-ray curable compound is cured through a radical polymerization reaction,

and specifically a step of irradiating ultraviolet rays using a carbon arc lamp, an electrodeless lamp, a mercury-vapor lamp, a xenon lamp, a fluorescent lamp and argon glow discharge as an ultraviolet source. Among others, the electrodeless lamp is preferred because it can irradiate light uniformly to a substrate to be coated, which has a complicated structure.

A substrate to be coated used in the method of forming a clear coating film of the present invention can include various base materials such as metal molded articles, plastic molded articles, foam substances and the like, and more specifically it can include molded articles of metals such as iron, aluminum and alloys thereof, anodized aluminum, brass, bronze, galvanized steel sheet, tin-plated steel sheet, nickel-plated steel sheet and chromium-plated steel sheet, and plastic molded articles. The method of forming a clear coating film of the present invention is particularly effective in the case where the substrate to be coated has both of an approximately horizontal plane and an approximately vertical plane. Accordingly, the method of forming a clear coating film of the present invention can be suitably used particularly for a coating method of a substrate to be coated, having a complicated shape, such as automotive bodies, automotive assembly parts and special-purpose vehicles.

The method of forming a clear coating film of the present invention may further includes the step (A-1) of applying an intermediate coating composition onto a cured electrodeposition coating film and heat curing the intermediate coating composition applied to form a multilayer coating film, and the step (A-2) of applying a base coating composition onto the above-mentioned multilayer coating film, prior to the step 1.

And, the method of forming a clear coating film of the present invention may further includes the step (B-1) of applying an intermediate coating composition onto a not-yet-cured electrodeposition coating film and heat curing the intermediate coating composition applied and the not-yet-cured electrodeposition coating film to form a multilayer coating film,

and the step (B-2) of applying a base coating composition onto the above-mentioned multilayer coating film, prior to the step 1.

The above-mentioned step (A-1) is a step of applying an intermediate coating composition onto a electrodeposition coating film formed on a substrate to be coated and heat curing the intermediate coating composition applied to form a multilayer coating film.

The method of forming a clear coating film of the present invention is preferably applied to metal molded articles on which cationic electrocoating can be performed. The above-mentioned substrate to be coated is preferably chemical conversion treated on its surface. Further, the substrate to be coated may be provided with an electrodeposition coating film. As a coating composition used in the above electrocoating, a cationic and an anionic coating compositions can be used, but a cationic electrodeposition coating composition is preferred from the viewpoint of an anti-corrosive property.

And, it is possible that the intermediate coating film has been formed on the electrodeposition coating film. The intermediate coating composition is used for forming the intermediate coating film. The above intermediate coating composition is not particularly limited and it can include a water-borne intermediate coating composition or an organic solvent type intermediate coating composition well known to those skilled in the art. When the above intermediate coating composition is applied, the above electrodeposition coating film may be a not-yet-cured one. That is, the multilayer coating film may be formed by applying an intermediate coating composition onto a not-yet-cured electrodeposition coating film and heat curing the intermediate coating composition applied and the not-yet-cured electrodeposition coating film (step (B-1)).

As a method of heat curing the above intermediate coating composition, a publicly known method can be employed.

The above-mentioned steps (A-2) and (B-2) are a step of applying a base coating composition onto a multilayer coating film consisting of the electrodeposition coating film and the intermediate coating film.

The above-mentioned base coating composition is not particularly limited and it may include, for example, a film forming resin, a curing agent, an organic or an inorganic or a glorious material-containing coloring pigment and an extender. The form of the above base coating composition is not particularly limited and it can include a water-borne base coating composition or an organic solvent type base coating composition.

A method of coating the substrate, on which the above multilayer coating film is formed, with the above base coating composition is not particularly limited and it can include spray coating and rotary atomization type coating, and a multi-stage coating using these methods or a coating method of combining these methods is preferred from the viewpoint of improving an appearance.

The method of forming a clear coating film of the present invention may be a method of coating by 2 coating processes and 1 baking process in which a base coating composition is applied to a substrate to be coated to form a base not-yet-cured coating film, and then the above water-borne clear coating composition is applied onto the above base not-yet-cured coating film according to the above steps 1 to 3, and the above base not-yet-cured coating film and a clear not-yet-cured coating film are simultaneously heated and cured, or may be a method of coating by 2 coating processes and 2 baking processes in which the above base not-yet-cured coating film is heated and cured, and then the above water-borne clear coating composition is applied to form a clear not-yet-cured coat, and this clear not-yet-cured coating film is heated and cured.

When coating is performed by the 2 coating processes and 1 baking processes, a film thickness of the above base coating composition applied is preferably within a range of 10 μm (lower

limit) to 20 μm (upper limit) in terms of a dried film thickness.

In the method of forming a clear coating film of the present invention, when the above base coating composition is water-borne, it is desired to heat a base not-yet-cured coating film at 40°C to 100°C for 2 to 10 minutes before applying the above water-borne clear coating composition in order to obtain a good finished coating film.

The base not-yet-cured coating film formed by the above-mentioned method together with the clear not-yet-cured coating film obtained by the above step 1 and the above step 2 in the method of forming a clear coat of the present invention are simultaneously heated and cured in the above step 3, and thereby a multilayer coating film can be formed.

And, when a multilayer coating film is formed by the above-mentioned 2 coating processes and 2 baking processes, the multilayer coating film can be formed by performing the above steps 1 to 3 after heat curing the above base not-yet-cured coating film to form a clear coating film.

A heating temperature in heat curing the above base not-yet-cured coating film is preferably within a range of 100°C (lower limit) to 180°C (upper limit). And, the heating temperature more preferably has a lower limit of 120°C and an upper limit of 160°C. A heat curing time varies with a curing temperature, but it is proper to heat cure in 10 to 30 minutes when heat curing is carried out at the above heat curing temperature.

The method of forming a clear coating film of the present invention may also include a step (C) of further applying a overcoat clear coating composition to a coating film which has been subjected to the above step 3. The above-mentioned overcoat clear coating composition is intended for forming two or more layers of clear coating films when higher appearance is attained or a particle size of pigment in a base coating film is large. A method of forming those can include, for example, a method described in Japanese Kokai Publication Hei11-253877.

In accordance with the water-borne clear coating composition and the method of forming a clear coating film of the present invention, the sagging can be suitably controlled and a coating film, which can satisfy properties such as appearance performance required in a clear coating film, can be formed. That is, it is possible to improve the sagging while maintaining properties as a clear coating film, and thereby it is possible to obtain a clear coating film having an excellent appearance performance. And, the coating composition of the present invention has no problem of VOC and can reduce the environmental loads because of being water-borne.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, the present invention will be described in more detail by way of examples, but the present invention is not limited to these examples. In addition, "part(s)" and "%" refer to "part(s) by weight" and "% by weight" in Examples, unless otherwise specified.

(Production Example 1 Production of acrylic resin)

In a flask equipped with a condenser, a solvent recovery unit, a stirrer, a thermometer and a nitrogen gas inlet pipe, 40 parts of dipropyleneglycol monomethyl ether (DPM) was put, and the DPM was heated to 130°C and kept at this temperature, and then to this, a mixture of 15 parts of acrylic acid, 16 parts of hydroxyethyl methacrylate, 39 parts of ethyl acrylate, 5 parts of styrene and 5 parts of MSD-100 as monomers, and 20 parts of NK Ester M-90G (produced by SHIN-NAKAMURA CHEMICAL Co., Ltd.), 13 parts of an initiator Kayaester O (t-butylperoxyhexanoate, produced by Kayaku Akzo Corporation) and 10 parts of DPM was added dropwise over 3 hours. Then, the resulting mixture was stirred at 130°C for 30 minutes and to this, a solution formed by dissolving 0.3 part of Kayaester O in 5 parts of DPM was added dropwise over 30 minutes. After this, a temperature was reduced to 110°C and to this, 20 parts of CARDURA E10P (trade name, produced by Japan Epoxy Resins Co., Ltd.) and 2.6 parts of TBAH

(tetrabutylammonium hydroxide) were added and the mixture was stirred at 110°C to graft the mixture. After an acid value reached 58.8, all of the solvent was eliminated and the solution was neutralized with 100% DMEA and then deionized water was added. A solid content of the resulting acrylic resin solution was 44.8 weight % and a number-average molecular weight by GPC was 3000.

(Example 1)

TINUVIN 384 (ultraviolet absorber produce by CIBA-GEIGY Corporation) 2 parts, 2 parts of TINUVIN 292 (light stabilizer produced by CIBA-GEIGY Corporation), and 2 parts of an acrylic surface control agent (solid content 50 weight %) produced by NIPPON PAINT Co., Ltd. were mixed to obtain an additive solution.

The acrylic resin, obtained in Production Example 1, 178 parts, 22 parts of Cymel 327 (melamine produced by Mitsui Cytec, Ltd.), 10 parts of A-TMM-3L (special acrylate produced by SHIN-NAKAMURA CHEMICAL Co., Ltd.), and 2 parts of Darocur 1173 (photopolymerization initiator produced by CIBA-GEIGY Corporation) were stirred with Disper and mixed uniformly, and then to this, the above-mentioned additive solution obtained was added, and the resulting mixture was stirred to prepare a curable coating composition product. The obtained curable coating composition product was diluted with ion-exchange water in such a way that the viscosity of the coating composition by Ford cup No. 4 becomes 40 seconds at 20°C.

A cationic electrodeposition coating POWERTOP PU-50 (trade name) produced by NIPPON PAINT Co., Ltd. was electrocoated on a dull steel sheet having a size of 300 mm in length, 100 mm in width and 0.8 mm in thickness, treated with zinc phosphate, in such a way that a dried film thickness is about 25 μm, and onto this, Orga P-2 Sealer (trade name) produced by NIPPON PAINT Co., Ltd. was air sprayed in such a way that a dried film thickness is about 40 μm and heat cured at 140°C for 30 minutes. To this coated test plate, a black colored water-borne base coating composition was air sprayed in such a way that a dried film thickness is 16 μm and the coated test plate was heat cured at

140°C for 30 minutes. Further, the coated test plate was honed with a No. 1000 sand paper and wiped with a cloth impregnated with petroleum benzin to degrease to obtain a coated test plate.

This coated test plate was placed with a longitudinal direction vertical, and the above-mentioned coating composition prepared was air sprayed onto an upper area of the test plate, which is 70 mm in height, in such a way that a dried film thickness is about 40 μm, and immediately ultraviolet rays were irradiated to the test plate in the conditions of a bulb type of an H bulb, a conveyer speed of 4 m/minute and a lamp distance of 10 cm using an electrodeless lamp "F600 (240 W/cm)" manufactured by Fusion UV Systems Japan K.K. After irradiation, the test plate was placed with a longitudinal direction vertical and heat cured at 140°C for 30 minutes to obtain a test plate.

(Examples 2 to 14)

Based on the formulations in Table 1, each curable coating composition was prepared in the predetermined heating conditions in the same manner as in Example 1 and a test plate was obtained.

(Comparative Examples 1 to 4)

Based on the formulations in Table 2, each curable coating composition was prepared in the predetermined heating conditions in the same manner as in Example 1 and a test plate was obtained.

(Method of evaluation)

On the test plates obtained as described above, each coating film of the test plates obtained was evaluated according to the following evaluation method. The results of evaluations are shown in Tables 1 and 2.

(1) Measurement of viscosity

The same procedure as in Example was performed except for using a tin plate in place of the above coated test plate, and a coating film on the tin plate was scraped off before and after ultraviolet rays were irradiated, respectively, and the viscosity of each coat at 25°C was measured with an E type viscometer (VISCONIC EMD viscometer manufactured by TOKI SANGYO Co., LTD.).

(2) Evaluation of sagging

i) Tape sagging

The distance (mm), by which the coating composition at the coated area sagged in an uncoated area of 30 mm in width in the lower portion of the above coated test plate after heat curing, was measured.

ii) Hole sagging

The same procedure as in Example was performed except for using a test plate for testing the hole sagging, which has a size of 0.8 mm x 100 mm x 500 mm and ten holes of 10 mm in diameter, in place of the above coated test plate, and the distance (mm), by which the coating composition at the hole portion of the inclined test plate sagged from the bottom of the hole after heat curing, was measured and a film thickness within a sagging distance of 5 mm is shown in Tables 1 and 2.

(3) Pencil hardness

Pencil hardness was measured on the obtained coating film according to JIS K 5400.8.4.2.

(4) Appearance of coating film

The appearance of the cured coating film obtained was rated visually. Rating criteria are as follows.

◎: There is not the occurrence of wrinkling or cratering.

○: There are few occurrence of wrinkling or cratering.

△: There are a few occurrences of wrinkling or cratering.

×: There are many occurrences of wrinkling or cratering.

Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Formulation	Component a (water-borne acrylic resin)	Production Example 1 (80)	Production Example 1 (90)	Production Example 1 (70)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)
	Component b (melamine resin)	Cymel 327 (20)	Cymel 327 (10)	Cymel 327 (30)	MYCOAT 723 (20)	Cymel 327 (20)	Cymel 327 (20)	Cymel 327 (20)
	Component c (acrylate oligomer)	A-TMM-3L (10)	A-TMM-3L (10)	A-TMM-3L (10)	A-TMM-3L (10)	A-TMM-3L (20)	A-TMM-3L (5)	A-TMM-3L (10)
	Component d (photopolymerization initiator)	Darocur 1173 (2)	Darocur 1173 (2)	Darocur 1173 (2)	Darocur 1173 (2)	Darocur 1173 (2)	Darocur 1173 (2)	Darocur 1173 (1)
Results	Viscosity of a coating film before UV irradiation (mPa•s)	1000	1000	1000	1000	1000	1000	1000
	Viscosity of a coating film after UV irradiation (mPa•s)	60000	65000	70000	62000	88000	55000	50000
	Tape sagging (mm)	0	0	0	0	0	0	0
	Hole Sagging (mm)	36	24	41	36	34	27	33
	Pencil hardness	HB	B	F	HB	HB	HB	B
	Appearance of coating film (visual)	◎	◎	◎	◎	◎	◎	◎

		Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
Formulation	Component a (water-borne acrylic resin)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)
	Component b (melamine resin)	Cymel 327 (20)	Cymel 327 (20)	Cymel 327 (20)	Cymel 327 (20)	Cymel 327 (20)	Cymel 327 (20)	Cymel 327 (20)
	Component c (acrylate oligomer)	M-400 (10)	TMPTA (10)	D-330 (10)	A-TMM-3L (10)	A-TMM-3L (10)	A-TMM-3L (10)	A-TMM-3L (10)
	Component d (photopolymerization initiator)	Darocur 1173 (2)	Darocur 1173 (2)	Darocur 1173 (2)	Irgacure 184 (2)	Irgacure 184 (2)	Irgacure 184 (2)	Darocur 1173 (5)
Results	Viscosity of a coating film before UV irradiation (mPa•s)	1000	1000	1000	1000	1000	1000	1000
	Viscosity of a coating film after UV irradiation (mPa•s)	72000	52000	59000	77000	84000	61000	80000
	Tape sagging (mm)	0	0	0	0	0	0	0
	Hole Sagging (mm)	36	29	30	31	33	34	33
	Pencil hardness	HB	HB	B	HB	HB	HB	HB
	Appearance of coating film (visual)	◎	◎	◎	◎	◎	◎	◎

Numerical value in a parenthesis in Table represents parts by weight (solid matter).

A-TMM-3L: (pentaerithritol triacrylate produced by SHIN-NAKAMURA CHEMICAL Co., Ltd.)

M-400: (mixture of dipentaerithritol pentaacrylate and hexaacrylate, produced by TOAGOSEI Co., Ltd.)

D-330: (acrylate oligomer produced by Nippon Kayaku Co., Ltd.; Mn 584)

TMPTA: (trimethylolpropane triacrylate)

Darocur 1173: (photopolymerization initiator produced by Ciba Specialty Chemicals K.K.)

Irgacure 184: (photopolymerization initiator produced by Ciba Specialty Chemicals K.K.)

Table 2

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Formulation	Component a (water-borne acrylic resin)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)	Production Example 1 (80)
	Component b (melamine resin)	Cymel 327 (20)	MYCOAT 723 (20)	Cymel 327 (20)	Cymel 327 (20)
	Component c (acrylate oligomer)	A-TMM-3L (10)	A-TMM-3L (10)	D-330 (10)	M-400 (10)
	Component d (photopolymerization initiator)	None	None	None	None
Results	Viscosity of a coating film before UV irradiation (mPa•s)	1000	1000	1000	1000
	Viscosity of a coating film after UV irradiation (mPa•s)	1000	1000	1000	1000
	Tape sagging (mm)	30	30	30	30
	Hole Sagging (mm)	12	11	9	10
	Pencil hardness	HB	HB	HB	HB
	Appearance of coating film (visual)	◎	◎	◎	◎

From Tables 1 and 2, it was found that in the clear coating films obtained by the water-borne clear coating compositions of Examples, sagging was adequately inhibited and appearance performance was excellent.

On the other hand, in the clear coating films obtained by the water-borne clear coating compositions of Comparative Examples, sagging was not adequately inhibited.

INDUSTRIAL APPLICABILITY

The water-borne clear coating composition and the method of forming a clear coating film of the present invention are suitable for coating of automotive bodies, automotive parts and special-purpose vehicles, and thereby sagging can be inhibited while maintaining various properties required in a clear coating composition and thereby a clear coating film having an excellent appearance can be formed.

CLAIMS

1. A water-borne clear coating composition,
containing an active energy-ray curable compound having an unsaturated bond, a photopolymerization initiator, a water-borne acrylic resin and a melamine resin.

2. The water-borne clear coating composition according to Claim 1,
wherein the active energy-ray curable compound having an unsaturated bond is a compound having a (meth)acrylate group.

3. A method of forming a clear coating film,
comprising steps of applying the water-borne clear coating composition according to Claim 1 or 2 to a substrate to be coated (step 1),
irradiating active energy-rays to a not-yet-cured coating film obtained by the step 1 from an approximately vertical plane (step 2), and
heating the substrate to be coated, which has been subjected to the step 2, to give a cured coating film (step 3).

4. The method of forming a clear coating film according to Claim 3,
wherein the viscosity of the coating film which has been subjected to the step 2 is 2000 to 500000 mPa•s.

5. The method of forming a clear coating film according to Claim 3 or 4,
wherein said method comprises the step (A-1) of applying an intermediate coating composition onto a cured electrodeposition coating film and heat curing the intermediate coating composition applied to form a multilayer coating film, and the step (A-2) of applying a base coating composition onto said multilayer coating film, prior to the step 1.

6. The method of forming a clear coating film according to Claim 3 or 4,

wherein said method comprises the step (B-1) of applying an intermediate coating composition onto a not-yet-cured electrodeposition coating film and heat curing the intermediate coating composition applied and the not-yet-cured electrodeposition coating film to form a multilayer coating film, and the step (B-2) of applying a base coating composition onto said multilayer coating film, prior to the step 1.

7. The method of forming a clear coating film according to any one of Claims 3 to 6,

comprising a step (C) of applying a overcoat clear coating composition to the substrate after the step 3.

8. A coated substrate,

wherein a substrate to be coated is an automotive body or an automotive assembly part and said coated substrate is coated by the method according to any one of Claims 3 to 7.

INTERNATIONALSEARCHREPORT

International application No.
PCT/JP2006/312839

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C09D4/00(2006.01)i, B05D1/38(2006.01)i, B05D3/06(2006.01)i,
B05D7/24(2006.01)i, C09D133/00(2006.01)i, C09D161/28(2006.01)i

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. C09D4/00, B05D1/38, B05D3/06, B05D7/24, C09D133/00, C09D161/28

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2006
Registered utility model specifications of Japan 1996-2006
Published registered utility model applications of Japan 1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-245606 A (KANSAI PAINT CO.,LTD.) 2003.09.02, claims 1-3, [0024]-[0027][0033], family none	1-8
A	JP 11-300272 A (KANSAI PAINT CO.,LTD.) 1999.11.02, Claims 1-2, [0008][0022][0047][0048], family none	1-8
A	JP 1-011169 A (NOF CORPORATION) 1989.01.13, claims 1-7, examples 1-5, family none	1-8

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"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)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"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
"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
"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
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16.08.2006	29.08.2006

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INTERNATIONALSEARCHREPORT

International application No.
PCT/JP2006/312839

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2003/080745 A1 (BASF NOF COATINGS CO.,LTD.) 2003.10.02, claims 1-6, page 10, line 28, & JP 2003-277684 A & JP 2004-051944 A & JP 2004-149720 A & EP 1489148 A1 & US 2005/0165125 A1	1-8
A	JP 2002-080547 A (DAIKIN INDUSTRIES, LTD.) 2002.03.19, Claims 1-10, family none	1-8