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SPECIFICATION

Title of the Invention:

Multi-Pack Aqueous Coating Composition

Background of the Invention:(1) Field of the Invention:

The present invention relates to a multi-pack aqueous coating composition, more particularly a cold-drying multi-pack aqueous coating composition which is capable of forming a coating film showing good properties in weather resistance, durability, adhesion properties, and pollution resistance without reducing crosslinking properties. The coating composition of the present invention is applicable to coating of architectural interior and exterior decorations, bridges, ships, automobiles, vehicles, etc.

(2) Description of the Background Art:

A cold-drying aqueous coating composition is generally known to contain an acrylic copolymer emulsion as a vehicle component. The acrylic copolymer emulsion is such that a film is formed by fusion bonding between emulsion particles. However, it was difficult for a glass transition temperature of the copolymer to design at such a high level as to achieve the film-forming properties due to the above fusion bonding, resulting in that a coating film formed from an aqueous coating

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composition consisting of the above acrylic copolymer emulsion showed poor properties in pollution resistance and water resistance.

For the purpose of solving the problems produced at the time of forming a coating film from the emulsion of the above aqueous coating composition, Japanese Patent Application Laid-Open No. 249587/92 discloses a method of crosslinking between emulsion particles through a crosslinking agent having a relatively low molecular weight, resulting in improving film-forming properties, and in keeping weather resistance and initial drying properties in addition to pollution resistance and water resistance.

However, since the crosslinking reaction by use of the above crosslinking agent does not take place until the water contained in the coating composition has evaporated and the fusion bonding between emulsion particles has taken place, under the conditions of a low-temperature or high humidity, the evaporation of the water takes place so slowly that crosslinking does not proceed to be incomplete, resulting in producing such problems that a resulting film shows whitening and does not show intended performances.

On the other hand, Japanese Patent Publication No. 32851/96 discloses an isocyanate-curing type two-pack aqueous coating composition. However, use of the above aqueous coating composition provides adverse effects on

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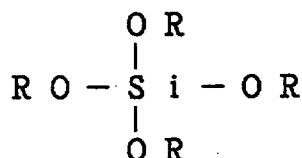


water resistance and pollution resistance to be impractical as a cold-drying coating composition.

Summary of the Invention:

It is an object of the present invention to provide a cold-drying multi-pack aqueous coating composition which is capable of forming a coating film showing good properties in weather resistance, durability, adhesion properties, pollution resistance, etc. without reducing crosslinking properties, particularly under the conditions of low temperature and high humidity.

That is, the present invention provides a multi-pack aqueous coating composition prepared by mixing (A) a base coating composition containing, as a binder component, a water-dispersible copolymer having a hydroxyl number of 5 to 200 mg KOH/g, (B) a crosslinking agent containing a compound having at least two isocyanate groups in one molecule in such an amount that the isocyanate group is contained in the range of 0.2 to 3.0 moles per one mole of the hydroxyl group contained in the base coating composition (A), and (C) an organosilicate represented by the following general formula:



where R is same or different and is hydrogen atom or a monovalent hydrocarbon group having 1 to 10 carbon atoms,

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and/or its condensate in the range of 0.1 to 50 parts by weight per 100 parts by weight of a total amount of a resin solid content of the base coating composition (A) and a solid content of the crosslinking agent (B).

Detailed Description of the Invention:

The water-dispersible copolymer used in the base coating composition (A) of the present invention includes polyol resins such as acrylic resin, polyester resin, polyurethane resin, silicone resin, fluorocarbon resin and the like having respectively a hydroxyl number of 5 to 200 mg KOH/g, preferably 10 to 100 mg KOH/g, an acid value of 0 to 300 mg KOH/g, preferably 0 to 150 mg KOH/g, a glass transition temperature of 0 to 80°C, preferably 10 to 60 °C, and a weight average molecular weight of 1,000 to 400,000, preferably 20,000 to 300,000, and preferably includes an acrylic emulsion obtained by subjecting a monomer mixture containing a hydroxyl group-containing monomer and other unsaturated monomer copolymerizable therewith to emulsion polymerization in the presence of an emulsifier.

When the hydroxyl number of the water-dispersible copolymer is less than 5 mg KOH/g, insufficient crosslinking points make film performances unsatisfactory. On the other hand, when more than 200 mg KOH/g, an initial water resistance is undesirably reduced and coating workability is undesirably reduced due to an increased viscosity of the coating composition. When the



acid value of the water-dispersible copolymer is more than 300 mg KOH/g, water resistance of the coating film is undesirably reduced. When the glass transition temperature of the water-dispersible copolymer is lower than 0°C, the coating film shows poor properties in water resistance and pollution resistance. On the other hand, when higher than 80°C, an excess amount of the plasticizer and organic solvent used for forming the coating film is needed, resulting in making an initial drying properties poor, and in easily developing cracks on the coating film with time.

When the weight average molecular weight of the water-dispersible copolymer is less than 1,000, the coating film shows poor properties in weather resistance and water resistance. On the other hand, when more than 400,000, poor compatibility with other components in the coating composition undesirably reduces film-forming properties and curing properties.

Examples of the hydroxyl group-containing monomer used in the water-dispersible copolymer include C₁₋₆ hydroxyalkyl esters of acrylic acid or methacrylic acid such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and the like; hydroxyalkyl vinyl ethers such as hydroxyethyl vinyl ether; equimolar adducts of C₂₋₂₀ glycols such as ethylene glycol or polyester polyols such as polyethylene glycol with unsaturated carboxylic acids such as (meth)acrylic acid, monoethers of polyether



polyols such as polyethylene glycol with hydroxyl group-containing monomers such as 2-hydroxyethyl (meth)acrylate, and the like. These monomers may be used singly or in combination.

Examples of the other unsaturated monomers used in the water-dispersible copolymer may include C_{1-24} alkyl esters or cycloalkyl esters of acrylic acid or methacrylic acid, for example, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, isobornyl (meth)acrylate, and the like; unsaturated carboxylic acid such as (meth)acrylic acid, sulfoethyl (meth)acrylate and sodium salt thereof or ammonium salt thereof; dimethyl aminoethyl (meth)acrylate, (meth)acrylamide; vinyl aromatic compounds such as styrene, α -methylstyrene, vinyltoluene and the like; vinyl acetate, vinyl chloride, vinyl ether, (meth)acrylonitrile; alkoxysilyl group-containing monomer such as vinyltrimethoxysilane, γ -(meth)acryloyloxypropyltrimethoxysilane and the like; perfluoroalkyl (meth)acrylate such as perfluorobutylethyl (meth)acrylate, perfluorooctylethyl (meth)acrylate and the like; fluoroolefin, and the like. These monomers are used singly or in combination.

The water-dispersible copolymer in the present invention is contained in a vehicle component of the base coating composition (A), as the solid content, in an



amount of 20% by weight or more, preferably 50% by weight or more, and more preferably 80% by weight or more. An above amount less than 20% by weight makes it impossible to obtain satisfactory coating film performances in water resistance, durability, etc.

The base coating composition of the present invention may optionally contain other resin emulsions such as vinyl acetate emulsion, acrylic resin emulsion, vinyl acetate-acrylic emulsion, ethylene-vinyl acetate emulsion, silicone-acrylic emulsion, epoxy resin emulsion, urethane resin emulsion, alkyd resin emulsion, polyurethane emulsion and the like. Examples of water-soluble resin to be used in combination may include water-soluble acrylic resin, polyvinyl alcohol, natural or synthetic rubber latex and the like. These may be used singly or in combination.

The above base coating composition (A) contains, as a film-forming assistant, a plasticizer and/or an organic solvent having a solubility parameter (hereinafter may be referred to as SP) of 8.0 to 9.8 in an amount of 1 to 50 parts by weight per 100 parts by weight of the resin solid content. When the SP is outside the above range, poor compatibility with the resin may cause separation in the coating composition.

Examples of the above plasticizer may include di-2-ethylhexyl phthalate, diisonyl phthalate, dibutyl phthalate, diisodecyl phthalate and the like. Examples of

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the above organic solvent may include alcohol based, ester based, ether based, hydrocarbon based solvents, for example, texanol, texanol isobutylate, butyl cellosolve, propylene glycol monomethyl ether, butyl carbitol, diisopropyl adipate and the like. These may be used singly or in combination. These are contained in the base coating composition (A) in an amount of 1 to 50 parts by weight, preferably 10 to 30 parts by weight per 100 parts by weight of the resin solid content. The above amount less than one part by weight causes to develop cracks on a coating film while being formed, resulting in making it impossible to obtain a uniform coating film. On the other hand, when more than 50 parts by weight, the coating film shows poor drying properties and may easily be polluted.

The base coating composition (A) may optionally contain additives for use in the coating composition, for example, pigments such as color pigments, extender pigments and the like; pigment dispersants, curing catalysts, anti-foaming agents, thickening agents, preservatives, anti-freezing agents, and the like.

Of these, the curing catalyst may include ones known in the art without particular limitations, for example, amine curing catalysts such as triethylamine, tripropylamine, tributylamine, diethanolamine, triethanolamine and the like; dibutyltin dilaurate, dibutyltin oxide, tin octylate, lead naphthenate, cobalt



naphthenate, and the like. Example of the anti-foaming agent may include polyether based ones, polysiloxane-polyether copolymer based ones, polysiloxane-silicic acid condensate based ones, metallic soap based ones, and the like.

The crosslinking agent (B) used in the present invention includes ones containing a compound having at least two isocyanate groups in one molecule, and may be added to the base coating composition (A) as it is or in combination with a surface active agent to be mixed with agitation, and may preferably include ones prepared by modifying the above polyisocyanate compound with a surface active agent or the like. The modified product may include ones prepared by introducing a hydrophilic chain without particular limitations, for example, (i) a reaction product between alkoxypolyalkylene glycol and a polyisocyanate compound as prepared by a method disclosed in Japanese Patent Publication No. 7472/80, (ii) a mixture of a polyisocyanate compound and an emulsifier prepared by reacting a polyisocyanate compound with alkoxypolyalkylene glycol and dialkanolamine as prepared by a method disclosed in Japanese Patent Application Laid-Open No. 10950/95, (iii) a reaction product of the reaction product (i) or the mixture (ii) with a silane coupling agent having hydroxyl group or amino group at one terminal and alkoxysilyl group at another terminal, or a mixture thereof as prepared by a method described in

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Japanese Patent Application No. 195836/96, and the like.

Examples of the polyisocyanate compound include aliphatic diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, and the like; alicyclic diisocyanates such as 4,4'-methylene-bis(cyclohexyl isocyanate), isophorone diisocyanate and the like; aromatic diisocyanates such as xylylene diisocyanate, tolylene diisocyanate, diphenylmethane diisocyanate, diphenylmethane diisocyanate (hereinafter referred to as polymeric MDI) and the like; and similar compounds such as isocyanurates, biurets and the like thereof. These may be used singly or in combination.

The reaction product (i) between alkoxypolyalkylene glycol and the polyisocyanate compound is a water-dispersible polyisocyanate prepared by reacting so that a remaining isocyanate content may in the range of 20 to 30% by weight, specifically by reacting alkoxypolyalkylene glycol and the polyisocyanate compound so that an equivalent ratio of isocyanate group to hydroxyl group may be in the range of 3 to 30, preferably 10 to 25. The alkoxypolyalkylene glycol may include ones represented by the general formula: $R_1O-(R_2O)_n-H$, where R_1 is alkyl group, R_2 is alkylene group, and n is 2 to 100, for example, methoxypolymethylene ether glycol, methoxypolyethylene ether glycol, ethoxypolyethylene ether glycol, ethoxypolybutylene ether glycol and the like, and

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may have a number average molecular weight of 100 to 4,000, preferably 400 to 2,000.

The mixture (ii) of the polyisocyanate compound and the emulsifier prepared by reacting the polyisocyanate compound with alkoxypolyalkylene glycol and dialkanolamine is a water-dispersible polyisocyanate composition, and a mixing ratio between the emulsifier and the polyisocyanate compound is such that an isocyanate content is 3 to 50% by weight, preferably 5 to 30% by weight. The mixture may partly be reacted.

The emulsifier is prepared by reacting the polyisocyanate compound and alkoxypolyalkylene glycol at an equivalent ratio of isocyanate group to hydroxyl group in the range of 3 to 30, preferably 10 to 25, followed by reacting with dialkanolamine so that an equivalent ratio of isocyanate group to amino group may be in the range of 0.5 to 2, preferably 0.8 to 1.2. The alkoxypolyalkylene glycol used in the preparation of the emulsifier may include the same ones as used in the above (i). Examples of the dialkanolamine may include dimethanolamine, diethanolamine, diisopropanolamine, diethanolaniline and the like.

The reaction product (iii) of the polyisocyanate in the reaction product (i) or the mixture (ii) with the silane coupling agent having hydroxyl group or amino group at one terminal and alkoxysilyl group at another terminal is such that a reaction between isocyanate group



of a hydrophilized polyisocyanate in the above (i) or (ii) and hydroxyl group or amino group in the silane coupling agent may be carried out at an equivalent ratio of isocyanate group to hydroxyl group or amino group in the range of 3 to 30 to obtain a reaction product having a remaining isocyanate content in the range of 3 to 50% by weight, preferably 5 to 30% by weight. When the above content is less than 3% by weight, a resulting coating film shows poor water resistance. On the other hand, when more than 50% by weight, the crosslinking agent shows poor water-dispersibility.

Examples of the silane coupling agent used in the preparation of the reaction product (iii) may include N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, N- β -(aminoethyl)- γ -aminopropylmethyldimethoxysilane, γ -aminopropyltriethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane and the like. The alkoxypolyalkylene glycol used in the preparation of the reaction product (iii) includes the same ones as in the above (i).

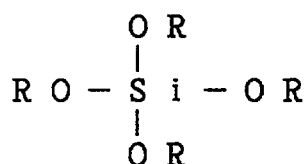
Of the above (i) to (iii), the (iii) well-balanced between hydrophilic properties and hydrophobic properties is preferred particularly from the standpoint of stability when water-dispersed.

The organosilicate and/or its condensate in the present invention include the organosilicate represented

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by the general formula:



where R is same or different and is hydrogen atom or a monovalent hydrocarbon group having 1 to 10 carbon atoms and/or its condensates. Use of such a silicon compound as to have a carbon number more than 10 in R results in reducing a speed of hydrolysis and in making poor pollution resistance of the film.

Examples of the monovalent hydrocarbon group having 1 to 10 carbon atoms in the above general formula may include alkyl group, aryl group and the like.

The above "alkyl group" may include straight-chain ones and branched ones, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neopentyl, n-hexyl, iso-hexyl, n-octyl and the like. Of these, lower alkyl groups having 1 to 3 carbon atoms are preferred. The "aryl group" may include monocyclic and polycyclic ones, for example, phenyl group, toluyl group, xylyl group, naphtyl group and the like, phenyl group being preferred.

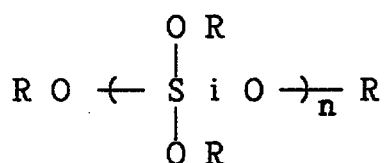
Preferable examples of the organosilicate used in the present invention may include tetrahydroxysilane, tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, tetraphenoxysilane, dimethoxydiethoxysilane and the like. These may be used

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alone or in combination.

The condensate of organosilicate may include branched or straight-chain condensates between the organosilicates represented by the above general formula and preferably includes condensates having a degree of condensation of 2 to 100 and represented by the general formula:



where R is defined as above, n is an integer of 2 to 100.

In the above general formula, when n is more than 100, effect of pollution resistance is undesirably reduced.

The organosilicate used in the present invention may preferably include such ones that R in the general formula is a lower alkyl group having 1 to 3 carbon atoms, and the condensate thereof may particularly include such ones that R in the general formula is a lower alkyl group having 1 to 3 carbon atoms and that the degree of condensation is in the range of 2 to 10.

A mixing ratio of the organosilicate and the condensate thereof is in the range of about 0.1 to 50 parts by weight, preferably about 1 to 40 parts by weight per 100 parts by weight of a total amount of a resin solid content in the base coating composition (A) and a solid content in the crosslinking agent (B). When the amount of the organosilicate and the condensate thereof is less than about

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0.1 part by weight, the film shows undesirably poor pollution resistance. On the other hand, when more than about 50 parts by weight, the film may be hardened and may undesirably result defects such as cracking, reduction in gloss and the like.

The multi-pack aqueous coating composition of the present invention is such that the surface of the finally formed cured film is treated with acid, so that the resulting film surface may have a contact angle to water of 70° or less, preferably 20 to 65° . The contact angle is a value obtained by such a manner that a coating film immediately after curing is dipped and treated with a 2.5 wt% aqueous sulfuric acid solution at 20°C for 24 hours, followed by washing an aqueous sulfuric acid solution adhered onto the film with water, drying, dropping a 0.03cc deionized water drop onto the film surface, and by measuring a contact angle to water of the water drop 3 minutes after at 20°C by use of a contact angle meter DCAA marketed by Kyowa Chemical Co., Ltd. When the contact angle is more than 70° , the coating film shows poor properties in pollution resistance and durability.

The multi-pack aqueous coating composition of the present invention is such that the multi-pack aqueous coating composition is coated onto a substrate, followed by drying at room temperature to form a cured film. When exposed outdoors, a contact angle to water of the film surface is slowly reduced due to an acid ingredient such as

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an acid rain, and the film surface is prevented from being polluted.

According to the present invention, it is preferred that the film is treated with an acid beforehand prior to being exposed outdoors. The acid pretreatment results in making it possible to prevent pollution of the film surface from the beginning.

The acid treatment of the film is carried out to such an extent that the film surface shows a contact angle to water of 70° or less, preferably 20 to 65° . The method of the acid treatment may not particularly be limited so long as the above conditions are satisfied, but specifically the film may preferably be treated in an acidic aqueous solution having a pH of 6 or less at about 5°C to 98°C . Examples of particularly preferable acid to be used may include inorganic acids such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid and the like. Preferably, the acidic aqueous solution adhered onto the treated film is removed. The contact angle may be measured in the same manner as above described.

The multi-pack aqueous coating composition of the present invention consists of the base coating composition (A), the crosslinking agent (B) and the organosilicate and/or its condensate (C), and is used by mixing the above components prior to use in such amounts that the isocyanate group contained in the crosslinking agent (B) is in the range of 0.2 to 3.0 moles, preferably 0.5 to 2.5 moles per

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one mole of the hydroxyl group contained in the base coating composition (A), and that the organosilicate and/or its condensate (C) is in the range of 0.1 to 50 parts by weight per 100 parts by weight of a total amount of the resin solid content in the base coating composition (A) and the solid content in the crosslinking agent (B).

The multi-pack aqueous coating composition of the present invention may be used in any pack type provided that the composition contains the base coating composition (A), the crosslinking agent (B) and the organosilicate and/or its condensate (B), for example, three-pack type to simultaneously mix the components (A), (B), and (C), two-pack type to mix a mixture of the components (A) and (C) with the component (B), and two-pack type to mix a mixture of the component (B) and (C) with the component (A).

The multi-pack aqueous coating composition may be coated onto various kinds of substrates by the coating method known in the art, for example, spray coating, roller coating, brushing, dip coating, etc. A coverage of the coating composition is not particularly limited, but suitably in the range of about 50 to 400 g/m².

The coating composition of the present invention is coated and dried at room temperature to form a coating film having good properties in weather resistance, durability, adhesion properties and pollution resistance without reducing crosslinking properties.

The present invention will be explained more in detail

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by the following Examples, in which "part" and "%" represent "part by weight" and "% by weight" respectively.

Preparation Examples of Water-Dispersible Copolymer:

Preparation Example 1

A 2-liter four-necked flask equipped with stirrer, thermometer, reflux tube and nitrogen inlet tube was charged with 309 parts of deionized water and 1.1 parts of Newcol 707SF (Nippon Nyukazai Co., Ltd., trade name, anionic surfactant, solid content: 30%), followed by keeping at 85 °C while purging with nitrogen, adding 21 parts of a preemulsion prepared by emulsifying the following composition and 0.32 part of ammonium persulfate, and 20 minutes after dropping a remaining amount of the preemulsion over 4 hours.

deionized water	325 parts
Newcol 707SF	43.3 parts
methyl methacrylate	45.5 parts
styrene	130 parts
n-butyl methacrylate	201.5 parts
2-ethylhexyl methacrylate	201.5 parts
2-hydroxyethyl methacrylate	65 parts
acrylic acid	6.5 parts
ammonium persulfate	1.3 parts

Completion of the above dropping procedure was followed by keeping at 85 °C for 2 hours, cooling down to 40°C, and controlling pH at 8.5 with ammonia water to obtain a water-dispersible copolymer (a) having a solid content of 50% and

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a weight average molecular weight of 150,000.

Preparation Example 2

A 4-liter four-necked flask equipped with stirrer, thermometer, reflux tube and nitrogen inlet tube was charged with 656.5 parts of 1-methoxy-2-propanol, followed by purging with nitrogen, keeping at 110°C with agitation, and dropping the following composition.

styrene	130 parts
n-butyl methacrylate	195 parts
2-ethylhexyl methacrylate	195 parts
2-hydroxyethyl methacrylate	65 parts
acrylic acid	65 parts
azobisisobutyronitrile	6.5 parts

Completion of the above dropping was followed by keeping at 110°C for 2 hours, cooling down to 40°C, adding 875.3 parts of deionized water to be water dispersed, and controlling pH at 8.5 with ammonia water to obtain a water-dispersible copolymer (b) having a solid content of 30% and a weight average molecular weight of 40,000.

Preparation of the Crosslinking Agent:

Preparation Example 3

A four-necked flask equipped with stirrer, thermometer, reflux tube and nitrogen inlet tube was charged with 225 parts of methoxypolyethylene ether glycol having a number average molecular weight of 550 and 871 parts of 1, 6-hexamethylene diisocyanate, followed by purging with nitrogen, reacting at 70 °C for 6 hours, subjecting a

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resulting reaction mixture to a thin film distillatory apparatus, and removing unreacted 1, 6-hexamethylene diisocyanate to obtain a monoisocyanate compound having methoxypolyethylene ether glycol residual group.

Separately, the same flask as above was charged with 37 parts of diethanolamine, followed by purging with nitrogen, and slowly dropping 250 parts of the monoisocyanate having methoxypolyethylene ether glycol residual group and prepared as above while being air-cooled so that a reaction temperature may be within 70°C. Completion of the above dropping was followed by stirring at 70°C for about one hour to find out disappearance of isocyanate group and to obtain an emulsifier.

Separately, the same flask as above was charged with 42 parts of the above emulsifier and 358 parts of Takenate D170HN (Trade name of trimer of 1, 6-hexamethylene diisocyanate, marketed by Takeda Chemical Industries Ltd.), followed by adding 12 parts of N- β -(aminoethyl)- γ -aminopropyl-trimethoxysilane, and stirring at 70 °C for 6 hours to obtain a crosslinking agent containing a water-dispersible polyisocyanate having an isocyanate group content of 17.7%, and having a viscosity of 800 cps.

Preparation Example of Dispersed Pigment Paste:

A 4-liter stainless steel vessel was charged with starting materials having the following formulation, followed by stirring with a disper for 30 minutes to obtain a dispersed pigment paste.

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potable water	960 parts
NOPCOSANT K (Trade name, marketed by SAN NOPCO Co., Ltd., pigment dispersant)	48 parts
Adekanol VH 420 (Trade name, marketed by Asahi Denka Kogyo K.K., thickening agent)	16 parts
SN Defoamer A63 (Trade name, marketed by SAN NOPCO Co., Ltd., anti-foaming agent)	32 parts
titanium white	3520 parts
ethanol	288 parts

Preparation Examples of Base Coating

Compositions (A₁) to (A₃):

One-liter stainless steel vessel was charged with the following formulations, followed by mixing respective components such as the dispersed pigment paste, the water-dispersible copolymer (a) and the like with agitation to prepare the base coating compositions (A₁) to (A₃).

Preparation Example of Base Coating Composition (A₁)

dispersed pigment paste prepared	280 parts
as above	
the above water-dispersible	490 parts
copolymer (a)	
Texanol (film-forming assistant)	28 parts
SN Defoamer A63 (the above	4.9 parts
trade name)	

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25% ammonia water	0.7 part
Primal (Trade name, marketed by Rohm & Haas A.G., thickening agent)	4.2 parts
SURAOFU S (Trade name, marketed by Takeda Chemical Industries Ltd., rotproof agent)	0.7 part

potable water	175 parts
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Preparation Example of Base Coating Composition (A₂)

dispersed pigment paste prepared as above	280 parts
the above water-dispersible copolymer (b)	817 parts
SN Defoamer A63 (the above trade name)	4.9 parts

25% ammonia water	0.7 part
Primal TT-935 (the above trade name)	4.2 parts
SURAOFU S (the above trade name)	0.7 part

Preparation Example of Base Coating Composition (A₃)

dispersed pigment paste prepared as above	280 parts
LS 2058 (Trade name, marketed by Bayer A.G., acrylic-modified polyester dispersion, solid content: 45%, hydroxyl number: 158 mg KOH/g)	544 parts
SN Defoamer A63 (the above trade name)	4.9 parts
25% ammonia water	0.7 part

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Primal TT-935 (the above trade name)	4.2 parts
SURAOFU S (the above trade name)	0.7 part
potable water	121 parts

Example 1

A mixture of 100 parts by weight as the resin solid content, of the above base coating composition (A₁), 5 parts by weight of Ethyl Silicate 48 (Trademark, marketed by Colcote Co., Ltd., lower condensate of tetraethyl silicate) and 18 parts by weight of the above crosslinking agent prepared in Preparation Example 3 was stirred to obtain an aqueous coating composition.

Example 2

Firstly, 5 parts by weight of Ethyl Silicate 48 (the above trademark) and 18 parts by weight of the above crosslinking agent prepared in Preparation Example 3 were dissolved in 23 parts by weight of SWASOL #1000 (Trade name, organic solvent, marketed by Maruzen Petroleum Co., Ltd.) to prepare a crosslinking agent solution. Thereafter, to 100 parts by weight, as the resin solid content, of the above base coating composition (A₁) was added 46 parts by weight of the above crosslinking agent solution, followed by stirring to obtain an aqueous coating composition.

Example 3

Firstly, 10 parts by weight of Ethyl Silicate 48 (the above trade mark) and 18 parts by weight of the crosslinking agent prepared in Preparation Example 3 were

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dissolved in 28 parts by weight of SWASOL #1000 (the above trade name) to prepare a crosslinking agent solution. Thereafter, to 100 parts by weight, as the resin solid content, of the above base coating composition (A₁) was added 56 parts by weight of the above crosslinking agent solution, followed by stirring to obtain an aqueous coating composition.

Example 4

Firstly, 5 parts by weight of Ethyl Silicate 40 (Trademark, marketed by Colcote Co., Ltd., lower condensate of tetraethyl silicate) and 18 parts by weight of the crosslinking agent prepared in Preparation Example 3 were dissolved in 23 parts by weight of SWASOL #1000 (the above trade name) to prepare a crosslinking agent solution. Thereafter, to 100 parts by weight, as the resin solid content, of the base coating composition was added 46 parts by weight of the above crosslinking agent solution, followed by stirring to obtain an aqueous coating composition.

Example 5

Firstly, 5 parts by weight of Ethyl Silicate 51 (Trademark, marketed by Colcote Co., Ltd., lower condensate of tetramethyl silicate) and 18 parts by weight of the crosslinking agent prepared in Preparation Example 3 were dissolved in 23 parts by weight of SWASOL #1000 (the above trade name) to prepare a crosslinking agent solution. Thereafter, to 100 parts by weight, as the resin solid content, of the base coating composition (A₁) was added 46



parts by weight of the above crosslinking agent solution, followed by stirring to obtain an aqueous coating composition.

Example 6

Firstly, 5 parts by weight of Ethyl Silicate 48 (the above trademark) and 18 parts by weight of the crosslinking agent prepared in Preparation Example 3 were dissolved in 23 parts by weight of SWASOL #1000 (Trademark, marketed by Maruzen Petroleum Co., Ltd., organic solvent) to prepare a crosslinking agent solution. Thereafter, to 100 parts by weight, as the resin solid content, of the above base coating composition (A₂) was added 46 parts by weight of the above crosslinking agent solution, followed by stirring to obtain an aqueous coating composition.

Example 7

Firstly, 5 parts by weight of Ethyl Silicate 48 (the above trademark) and 67 parts by weight of the crosslinking agent prepared in Preparation Example 3 were dissolved in 72 parts by weight of SWASOL #1000 (the above trade name) to prepare a crosslinking agent solution. Thereafter, to 100 parts by weight, as the resin solid content, of the above base coating composition (A₃) was added 144 parts by weight of the crosslinking agent solution, followed by stirring to obtain an aqueous coating composition.

Comparative Example 1

To 100 parts by weight, as the resin solid content, of the base coating composition (A₁) was added 18 parts by

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weight of the crosslinking agent prepared in Preparation Example 3, followed by stirring to obtain an aqueous coating composition.

Comparative Example 2

ALES CELA RETAN (Trade name, marketed by Kansai Paint Co., Ltd., non-pollution type ceramic-modified acrylic isocyanate curable solvent type white coating composition)

Comparative Example 3

ALES AQUA RETAN (Trade name, marketed by Kansai Paint Co., Ltd., one-pack reactively curable aqueous urethane white coating composition)

Preparation of Test Panels

VP Sealer White (Trade name, marketed by Kansai Paint Co., Ltd., solvent type sealer) was coated by roller coating to be a coverage of 100 g/m² onto a slate panel (90 mm × 300 mm × 6 mm), followed by drying to prepare a coated slate panel, coating twice thereonto respective coating compositions prepared in Examples 1-7 and Comparative Examples 1-3 by spray coating to be a coverage of 150 g/m², and drying at room temperature for 7 days to prepare respective test panels, which were subjected to the following tests for evaluation. Test results are shown in Table 1.

Test methods shown in Table 1 are as follows.

Film Appearance: Film surface was visually evaluated as follows.

4: The film shows no defects such as crazing, flashing,

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flaking and the like.

3: The film shows a little development of crazing and flaking.

2: The film shows some development of crazing, flashing and flaking.

1: The film shows remarkable development of crazing, flashing and flaking.

Gloss on Film Surface: Measurements of 60° specular reflection percentage were made.

Contact Angle to Water Prior to Acid Treatment:

It shows a value obtained by such a measuring method that a water drop of a 0.03 cc deionized water was dropped onto the surface of a film immediately after being formed, followed by measuring a contact angle three minutes after at 20 °C by a contactangle meter DCAA marketed by Kyowa Chemical Co., Ltd.

Contact Angle to Water after Acid Treatment:

A, film immediately after being formed was dipped into a 2.5 wt% aqueous sulfuric acid solution at 20°C for 24 hours, followed by washing the adhered aqueous sulfuric acid solution with water, drying, and measuring a contact angle in the same manner as above.

Adhesion Properties: A test was made by forming 100 squares (1 mm × 1 mm) according to the cross cut tape test as defined in JIS K-5400 8.5.2, followed by adhering thereonto an adhesive collophane tape, separating the tape and examining a degree of peeling off the squares.

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3: None of the squares is peeled off.

2: Corners of some squares are peeled off.

1: One third or more of the squares are peeled off.

Color Difference: A color difference between before and after exposure was determined as ΔL (difference in lightness) according to JIS Z-8730.

Pollution Appearance: Degree of pollution on the surface of the film was visually evaluated as follows.

3: Excellent with little or no pollution.

2: Good with little pollution.

1: Bad with remarkable pollution.



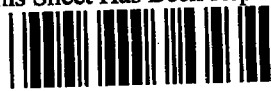


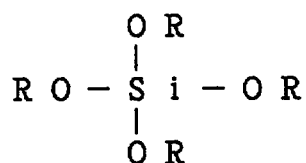
Table 1

		Examples							Comparative Examples		
		1	2	3	4	5	6	7	1	2	3
Film before outdoor exposure	Film appearance	4	4	4	4	4	4	4	4	4	4
	Gloss on film surface	84	87	76	86	87	88	88	90	80	85
	Contact angle to water before exposure	82	82	82	81	80	82	81	91	82	75
	Contact angle to water after acid treatment	55	55	55	54	53	55	54	87	58	62
	Adhesion properties	3	3	3	3	3	3	3	3	3	3
Film after outdoor exposure	Film appearance	4	4	4	4	4	4	4	4	4	4
	Gloss on film surface	80	82	74	81	81	83	83	80	75	70
	Color difference	1.50	1.20	1.50	1.50	1.40	1.20	1.30	5.00	1.10	7.10
	Pollution appearance	3	3	3	3	3	3	3	2	3	2
	Adhesion properties	3	3	3	3	3	3	3	3	3	3
Film after outdoor exposure	Film appearance	4	4	4	4	4	4	4	4	4	4
	Gloss on film surface	75	79	70	77	78	80	80	75	72	60
	Color difference	2.20	2.10	2.30	2.30	2.20	2.10	2.20	9.10	2.00	12.0
	Pollution appearance	3	3	3	3	3	3	3	2	3	2
	Adhesion properties	3	3	3	3	3	3	3	3	3	3



What is claimed is:

1. A multi-pack aqueous coating composition prepared by mixing (A) a base coating composition containing, as a binder component, a water-dispersible copolymer having a hydroxyl number of 5 to 200 mg KOH/g, (B) a crosslinking agent containing a compound having at least two isocyanate groups in one molecule in such an amount that the isocyanate group is contained in the range of 0.2 to 3.0 moles per one mole of the hydroxyl group contained in the base coating composition (A), and (C) an organosilicate represented by the following general formula:



where R is same or different and is hydrogen atom or a monovalent hydrocarbon group having 1 to 10 carbon atoms, and/or its condensate in the range of 0.1 to 50 parts by weight per 100 parts by weight of a total amount of a resin solid content of the base coating composition (A) and a solid content of the crosslinking agent (B).

2. A coating composition as claimed in claim 1, wherein the water-dispersible copolymer is a polyol resin selected from the group consisting of acrylic resin, polyester resin, polyurethane resin, silicone resin and fluorocarbon resin having a hydroxyl number of 5 to 200 mg KOH/g, an acid value of 0 to 300 mg KOH/g, a glass transition temperature of 0 to 80°C, and a weight average molecular weight of 1,000

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to 400,000 respectively.

3. A coating composition as claimed in claim 1, wherein the water-dispersible copolymer is an acrylic emulsion prepared by subjecting a monomer mixture of a hydroxyl group-containing monomer and other unsaturated monomer copolymerizable therewith to emulsion polymerization in the presence of an emulsifier.

4. A coating composition as claimed in claim 1, wherein the base coating composition (A) further contains a film-forming assistant selected from the group consisting of a plasticizer and an organic solvent, and having a solubility parameter of 8.0 to 9.8.

5. A coating composition as claimed in claim 1, wherein the crosslinking agent is selected from the group consisting of (i) a reaction product between alkoxypolyalkylene glycol and a polyisocyanate compound, (ii) a mixture of a polyisocyanate compound and an emulsifier prepared by reacting a polyisocyanate compound with alkoxypolyalkylene glycol and dialkanolamine, and (iii) a reaction product of the reaction product (i) or the mixture (ii) with a silane coupling agent having hydroxyl group or amino group at one terminal and alkoxysilyl group at another terminal, or a mixture thereof.

6. A coating composition as claimed in claim 1, wherein the coating composition is a cold-drying coating composition.

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