

DESCRIPTION

AQUEOUS EMULSION RESIN COMPOSITION AND COATING MATERIALS CONTAINING SAME

TECHNICAL FIELD

[0001]

The present invention relates to an aqueous emulsion resin composition and coating materials containing same.

BACKGROUND ART

[0002]

Buildings and structures are coated with coating materials excellent in weather resistance and stain resistance so that the beautiful appearances thereof can be maintained. Aqueous emulsion resin compositions obtained by emulsion polymerization of an unsaturated monomer composition containing 0.1 to 2 wt% of a silane coupling agent in the presence of an alkylalkoxysilane compound having 1 to 3 hydrolyzable alkoxy groups or a hydrolysate thereof, an alkoxysilane compound having four hydrolyzable alkoxyl groups or a hydrolysate thereof, and a nonionic compound having an OH-terminated polyalkylene glycol chain at a specific ratio have been proposed. (For example, see Patent Literature 1.) The aqueous emulsion resin compositions are excellent in weather resistance and stain resistance, but do not have sufficient long-term storage stability.

[0003]

[Patent Literature 1] Japanese Patent Application Laid-Open No. 2008-120904

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

[0004]

Therefore, the problem to be solved by the present invention is to provide an aqueous emulsion resin composition with excellent weather resistance, stain resistance, and

long-term storage stability and coating materials containing same.

SOLUTION TO PROBLEM

[0005]

As a result of keen study, the inventors of the present application found that an aqueous emulsion resin composition obtained by emulsion polymerization of an unsaturated monomer composition having a specific constitution in the presence of a specific surfactant with excellent long-term storage stability as well as weather resistance and stain resistance to complete the present invention.

Namely, the present invention relates to an aqueous emulsion resin composition obtained by emulsion polymerization of an unsaturated monomer composition comprising (A) γ -methacryloxypropyl trimethoxysilane, (B) cyclohexyl methacrylate, and (C) at least one unsaturated monomer selected from the group consisting of methyl methacrylate, butyl (meth)acrylate and 2-ethylhexyl (meth)acrylate in the presence of a free-radical reactive surfactant, wherein the unsaturated monomer composition contains 0.1 to 2 wt% of (A) γ -methacryloxypropyl trimethoxysilane and 25 to 75 wt% of (B) cyclohexyl methacrylate.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0006]

The present invention can provide an aqueous emulsion resin composition excellent weather resistance, stain resistance, and long-term storage stability.

DESCRIPTION OF THE EMBODIMENTS

[0007]

The present invention will be explained in detail below.

The aqueous emulsion resin composition of the present invention is obtained by emulsion polymerization of an unsaturated monomer composition comprising as essential

components γ -methacryloxypropyl trimethoxysilane as component (A), cyclohexyl methacrylate as component (B), and at least one unsaturated monomer selected from the group consisting of methyl methacrylate, butyl (meth)acrylate and 2-ethylhexyl (meth)acrylate as component (C) in the presence of a free-radical reactive surfactant. Not only weather resistance and stain resistance but also long-term storage stability can be significantly increased, due to the synergistic action of these components (A) to (C) in the present invention.

[0008]

γ -Methacryloxypropyltrimethoxysilane as component (A) has three hydrolyzable alkoxy groups and one unsaturated group and can impart excellent weather resistance and stain resistance to the aqueous emulsion resin composition of the present invention, due to its high self-crosslinking properties.

γ -Methacryloxypropyltrimethoxysilane is contained essentially in an amount of 0.1 to 2 wt%, preferably 0.2 to 1 wt% in the unsaturated monomer composition. If the content of γ -methacryloxypropyl trimethoxysilane is less than 0.1 wt%, weather resistance and stain resistance are decreased. If it is more than 2 wt%, polymerization stability and film-forming properties are decreased.

[0009]

Cyclohexyl methacrylate as component (B) can impart mainly weather resistance and stain resistance to the aqueous emulsion resin composition of the present invention.

Cyclohexyl methacrylate is contained essentially in an amount of 25 to 75 wt%, preferably 25 to 70 wt% in the unsaturated monomer composition. If the content of cyclohexyl methacrylate is less than 25 wt%, weather resistance and stain resistance are decreased. If it is more than 75 wt%, polymerization stability and film-forming properties are decreased.

[0010]

The unsaturated monomer as component (C) is at least one

monomer selected from the group consisting of methyl methacrylate, butyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate. Component (C) can mainly impart weather resistance and stain resistance to the aqueous emulsion resin composition of the present invention.

Component (C) is preferably contained in an amount of 30 to 70 wt%, more preferably 35 to 68 wt% in the unsaturated monomer composition.

[0011]

Various unsaturated monomers other than components (A) to (C) may be contained in the unsaturated monomer composition such that the effects of the present invention are not reduced. These unsaturated monomers include (meth)acrylates having a linear, branched, or cyclic alkyl chain with 1 to 18 carbon atoms such as methyl acrylate, ethyl (meth)acrylate, iso-butyl (meth)acrylate, tert-butyl (meth)acrylate, cyclohexyl acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, and isobornyl (meth)acrylate; aromatic vinyl compounds such as styrene, α -methylstyrene, p-methylstyrene, and ethylvinyl benzene; heterocyclic vinyl compounds such as vinylpyrrolidone; hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate; polyalkylene glycol (meth)acrylates such as ethylene glycol (meth)acrylate and butylene glycol (meth)acrylate; alkylamino (meth)acrylates such as N,N-dimethylaminoethyl (meth)acrylate and N,N-dimethylaminopropyl (meth)acrylate; vinyl ester compounds such as vinyl formate, vinyl acetate, vinyl propionate, and versatic acid vinyl (trade name); monoolefin compounds such as ethylene, propylene, butylene, and isobutylene; conjugated diolefin compounds such as butadiene, isoprene, and chloroprene; α,β -unsaturated mono- or dicarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, citraconic acid, itaconic acid, maleic acid, maleic anhydride, and fumaric acid; carboxyl group-containing vinyl compounds such as monohydroxyethyl (meth)acrylate phthalate and

monohydroxypropyl (meth)acrylate oxalate; amineimide group-containing vinyl compounds such as 1,1,1-trimethylamine methacrylimide; vinyl cyanide compounds such as acrylonitrile and methacrylonitrile; α,β -ethylenically unsaturated compounds containing an amide or substituted amide group such as (meth)acrylamide, N-methylacrylamide, N,N-dimethyl (meth)acrylamide, and N,N-dimethylaminopropyl (meth)acrylamide; carbonyl group-containing α,β -ethylenically unsaturated compounds such as acrolein, diacetone acrylamide, vinyl methyl ketone, and diacetone acrylate; sulfonic acid group-containing α,β -ethylenically unsaturated compounds such as allyl sulfonate and sodium p-styrene sulfonate; ethylenically unsaturated group-containing ultraviolet absorbers such as 3-(2H-benzotriazol-2-yl)-4-hydroxyphenetyl-methacrylate; ethylenically unsaturated group-containing light stabilizers such as 1,2,2,6,6-pentamethyl-4-pyperidyl methacrylate; and silane coupling agents containing an unsaturated group other than γ -methacryloxypropyl trimethoxysilane such as γ -methacryloxypropyltriethoxysilane, vinyltriethoxysilane, and vinyltris(β -methoxyethoxy)silane; and further include epoxy group-containing α,β -ethylenically unsaturated compounds such as glycidyl (meth)acrylate, 3,4-epoxycyclohexylmethyl (meth)acrylate, glycidyl vinyl ether, glycidyl (meth)allyl ether, and 3,4-epoxycyclohexyl (meth)acrylate; multifunctional vinyl compounds such as ethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, allyl (meth)acrylate, divinylbenzene, and diallyl phthalate, and the like. Regarding an epoxy group-containing α,β -ethylenically unsaturated compound and a multifunctional vinyl compound, the compounds per se can be crosslinked or can be crosslinked with an ethylenically unsaturated compound component having an active hydrogen group or a carbonyl group-containing α,β -ethylenically unsaturated compound (especially that having a keto group) is introduced and they are crosslinked in combination with a compound,

especially that having two or more hydrazide groups, i.e., a polyhydrazine compound such as oxalic dihydrazide, succinic dihydrazide, adipic dihydrazide, or polyacrylic hydrazide.

[0012]

Further, they can be crosslinked by adding a crosslinking compound without free-radical reactivity, for example, an alkyl silicate such as tetramethoxysilane, tetraethoxysilane, or methyltrimethoxysilane, a multifunctional epoxy compound such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol polyglycidyl ether, or bisphenol A glycidyl ether or the like during or after emulsion polymerization as necessary.

[0013]

In addition, the logical glass transition temperature (hereinafter, may be referred to as T_g) of the unsaturated monomer composition to be used preferably ranges from 0 to 50°C, considering prevention of blocking of coating film surfaces and film forming properties. The logical glass transition temperature in the present invention is a value calculated using the formulae below.

$$1/T_g(K) = W_1/T_1 + W_2/T_2 + W_3/T_3 + \dots W_n/T_n$$

$$T_g(^{\circ}C) = T_g(K) - 273$$

In the formula, W_1 , W_2 , W_3 , ... and W_n represent the ratio (wt%) of each unsaturated monomer to the unsaturated monomer composition. T_1 , T_2 , T_3 , ... and T_n represent the glass transition temperature (absolute temperature (K)) of a homopolymer of each unsaturated monomer. The glass transition temperature of a homopolymer of each unsaturated monomer is described in Polymer Hand Book (Second Edition, edited by J. Brandrup·E.H. Immergut).

[0014]

It is essential in the present invention to use a free-radical reactive surfactant in emulsion polymerization of components (A) to (C) and other unsaturated monomers added as necessary. The free-radical reactive surfactant can mainly impart weather resistance and stain resistance to the aqueous

emulsion resin composition of the present invention. Any free-radical reactive surfactants may be used without limitation as long as they have free-radical reactivity. Specific examples thereof include ADEKA REASOAP (registered trademark, manufactured by ADEKA Corporation), SE-10N, SR-10, SR-20, SR-30, ER-20, ER-30, and AQUARON (registered trademarks, manufactured by DAI-ICHI KOGYO SEIYAKU CO., LTD), HS-10, KH-5, KH-10, and ELEMNOL (registered trademarks, manufactured by Sanyo Chemical Industries, Ltd.), JS-20 and EMULGEN (registered trademarks, manufactured by KAO Corporation), PD-104, PD-420, PD-430, and the like.

The amount of free-radical reactive surfactant to be used is preferably 0.5 to 5 wt% with respect to the unsaturated monomer composition to be used. If the amount of free-radical reactive surfactant to be used is too small, the polymerization stability may be reduced. On the other hand, if it is too large, water-proof properties may be reduced. Basically, it is essential for these free-radical reactive surfactants to be added before or during emulsion polymerization so as to emulsify unsaturated monomers. However, post-addition thereof is allowed so as to impart stability to the emulsion that had been subjected to emulsion polymerization.

[0015]

Further, a surfactant without reactivity may be used in combination with the above free-radical reactive surfactant. Examples of a surfactant without reactivity that can be used in combination include anionic surfactants such as dodecyl sodium benzene sulfonate and dodecyl sodium sulfate; nonionic surfactants such as polyoxyethylene lauryl ether and polyoxyethylene nonylphenyl ether; cationic surfactants such as cetyl trimethyl ammonium bromide and lauryl pyridinium chloride; and amphoteric surfactants such as lauryl betaine. These surfactants without reactivity may be added before or during emulsion polymerization so as to emulsify unsaturated monomers or post-addition thereof is allowed so as to impart stability to the emulsion that had been subjected to emulsion

polymerization.

[0016]

In addition, polymerization initiators that can be used in emulsion polymerization include persulfate-based initiators such as potassium persulfate and ammonium persulfate; water-soluble azo-type initiators such as 2, 2'-azobis(2-methylpropionamidine) dihydrochloride; organic peroxides such as t-butyl hydroperoxide and cumene hydroperoxide; hydrogen peroxide and the like. These initiators may be used alone or in combination of two or more thereof. In general, the amount of polymerization initiator to be used is 0.1 to 1 wt% with respect to the unsaturated monomer composition to be used.

[0017]

Further, reducing agents may be used together with these polymerization initiators in emulsion polymerization as necessary. These reducing agents include reducing organic compounds such as ascorbic acid, tartaric acid, citric acid, glucose, and formaldehyde sulfoxylate metal salts; reducing inorganic compounds such as sodium thiosulfate, sodium sulfite, sodium bisulfite, and sodium metabisulfite; and the like. The amount of reducing agent to be used may be appropriately determined such that the effects of the present invention would not be reduced.

[0018]

In addition, a chain transfer agent may be used in emulsion polymerization as necessary. Examples of chain transfer agents include n-dodecylmercaptan, tert-dodecylmercaptan, n-butylmercaptan, 2-ethylhexyl thioglycolate, 2-mercaptoethanol, β -mercaptopropionic acid, and the like. The amount of chain transfer agent to be used may be appropriately determined such that the effects of the present invention would not be reduced.

[0019]

Emulsion polymerization in the present invention is generally performed under temperature conditions of about 5°C

to about 100°C, preferably about 50°C to 90°C. The reaction time is not particularly limited and can be appropriately changed, based on the amount of each component contained, the reaction temperature, and the like.

[0020]

Stability can be imparted to the aqueous emulsion resin composition by adding an acid or base to the aqueous emulsion resin composition obtained after emulsion polymerization to neutralize the pH thereof such that the pH becomes 4 to 10 and increasing the surface electric charge of the polymer. General acids that can be used include acetic acid, lactic acid, hydrochloric acid, phosphoric acid, sulfuric acid, and the like. In addition, general bases that can be used include amine compounds such as triethylamine, ammonia, diethanolamine, diethylaminoethanol and alkali metal hydroxides such as potassium hydroxide, sodium hydroxide, and lithium hydroxide.

[0021]

The coating materials of the present invention contain the above aqueous emulsion resin composition. A thickening agent, an antifoaming agent, a pigment (an extender, a color pigment, a hollow balloon, a thermal barrier pigment, and the like), a dispersing agent, a wetting agent, a light stabilizer, an ultraviolet absorber, a preservative, an antibacterial agent, and the like may be optionally added to the coating material of the present invention. The coating materials of the present invention may be used as various coating materials such as architectural paint, thermal barrier coating materials, heat-insulating coating materials, coating materials for siding boards, road marking coating materials, and mortar coating materials. In addition, the coating materials of the present invention may be used for materials that can be coated, i.e., paper, fibers, metal, wood, ceramics, and the like. The coating technique therefor is not limited.

EXAMPLES

[0022]

The present invention will be explained in detail, with reference to Examples and Comparative examples. Physical properties of the emulsions obtained in the Examples and the Comparative examples were evaluated by the methods described below.

[0023]

(1) Properties of an aqueous emulsion resin composition

(1-1) Nonvolatile components

An aqueous emulsion resin composition whose weight had been measured was dried at 105°C for one hour to determine the weight of residue after evaporation. The ratio (wt%) of nonvolatile components was calculated, based on the initial weight and the weight of the residue after evaporation.

(1-2) Viscosity

The viscosity of an aqueous emulsion resin composition was measured at 23°C at 60 rpm using a BM-type viscometer.

(1-3) pH

The pH of the aqueous emulsion resin composition was measured using a pH meter.

(1-4) Minimum film forming temperature (hereinafter, may be referred to as MFT)

MFTs were determined using a device for measuring heat-gradient minimum film forming temperature. In addition, the MFT of an aqueous emulsion resin composition which had been left at 50°C for one month was determined in the same manner.

[0024]

(2) Evaluation on long-term storage stability

The change rate of MFT was calculated, based on the initial MFT of the aqueous emulsion resin composition and the MFT of the aqueous emulsion resin composition which had been left, said MFTs having been determined as in (1-4). It was evaluated in accordance with evaluation standards below.

○: The change rate of MFT is 10% or less.

×: The change rate of MFT is more than 10%

[0025]

(3) Evaluation on weather resistance and stain resistance

(3-1) Preparation of gloss coating materials

82.6 parts by weight of deionized water, 0.8 part by weight of NATROSOL 250HR (manufactured by Hercules Corporation) as a thickening agent, 0.2 part by weight of ammonia water as a neutralizing agent, 1.1 parts by weight of AMORDEN FS-14D (manufactured by Daiwa Chemical Industry Co., Ltd.) as a preservative, 4.2 parts by weight of POIZ 521 (manufactured by KAO Corporation) as a dispersing agent, 1.1 parts by weight of SN DEFORMER 371 (manufactured by SAN NOPCO LIMITED) as an antifoaming agent, and 210 parts by weight of TIPAQUE CR-97 (manufactured by ISHIHARA SANGYO KAISHA, LTD.) as titanium oxide were fed into a container in this order, while agitated at about 2000 rpm using a homodisper. The mixture was further agitated at about 2000 rpm for one hour. Then, the mixture was filtered via a 120-mesh Teflon (registered trademark) mesh to obtain 300 parts by weight of a mill base having a solid content of 70 wt% (calculated, considering titanium oxide as a solid component).

300 parts by weight of the obtained mill base, 600 parts by weight of the aqueous emulsion resin composition (in the case where the weight ratio of the nonvolatile components was 50 wt%; in other cases where the weight ratio of the nonvolatile components was other than 50 wt%, the amount of the added resin was adjusted such that 300 parts by weight of the resin was contained in each composition, based on the weight of nonvolatile components), α parts by weight of CS-12 (manufactured by Chisso Corporation) as a film forming agent ($\alpha = \text{MFT} \div 5 \times 6$), and one part by weight of ADEKANOL UH-420 (manufactured by ADEKA Corporation) as a viscosity modifier were fed into another container and were agitated at about 2000 rpm for 10 minutes using a homodisper. Then, the mixture was filtered with 150-mesh Teflon (registered trademark) mesh to obtain 955 parts by weight of a gloss coating material having a solid content of 53.4 wt% and a pigment content of 15.5 vol% (calculated, considering the specific gravity of titanium oxide to be 4.2 and the specific gravity of the aqueous emulsion resin

composition to be 1.1).

[0026]

(3-2) Preparation of coated plates

The viscosity of the obtained gloss coating material was adjusted to about 800 mPa·s (measured using a BH-type viscometer at 20 rpm at 23°C) by adding water to the coating material. After a flexible board that had been subjected to a sealing treatment was sprayed with 150 g/m² of this coating material using a sprayer twice, the coated material was cured at 23°C at 65% in RH for one week to obtain a coated board. This procedural process was repeated to prepare two coated boards in total.

[0027]

(3-3) Evaluation on weather resistance

One of the prepared coated boards was tested using a Metaling Weather Meter (Suga Test Instruments) and the gloss retention after irradiation for 400 hrs was determined. An eight hour-cycle test comprising irradiation for two hours, irradiation for two minutes with water spraying (three cycles), and dew condensation for two hours (in the atmosphere at 30°C, at 95% in RH, and at a temperature of the coated board of 25°C) on conditions of using the Metaling Weather Meter of a black panel temperature of 63°C, humidity of 50% in RH, and an illumination intensity at 1.55 kW/m² was conducted. Weather resistance was evaluated in accordance with the standards below.

○: The gloss retention was 70% or higher.

△: The gloss retention was 50% or higher and less than 70%.

×: The gloss retention was less than 50%.

[0028]

(3-4) Evaluation on stain resistance

Another coated board prepared was exposed to the outside atmosphere for three months (Tatsuno City, Hyogo Prefecture, at 45° south latitude) and the color difference (ΔE) before and after the exposure was determined. The stain resistance was

evaluated in accordance with the standards below.

○: ΔE was less than 4.

△: ΔE was 4 or more and less than 8

×: ΔE was 8 or more.

[0029]

<Example 1>

200 parts by weight of deionized water and 0.2 part by weight of ADEKA REASOAP SR-10 (anionic reactive surfactant, manufactured by ADEKA Corporation) were fed into a polymerization apparatus equipped with an agitator, a thermometer, and a reflux condenser. After the space within the device was sufficiently filled with nitrogen, the temperature was raised to 75°C.

A mixture of 258 parts by weight of deionized water, 9.8 parts by weight of ADEKA REASOAP SR-10, 118 parts by weight of methyl methacrylate, 200 parts by weight of cyclohexyl methacrylate, 167 parts by weight of 2-ethylhexyl acrylate, 5 parts by weight of γ -methacryloxypropyl trimethoxysilane, and 10 parts by weight of methacrylic acid that had been emulsified using a homomixer was prepared. One portion (5 wt%) of the emulsified material was added to the inside of the polymerization apparatus, while the temperature in the polymerization apparatus was kept at 75°C.

Next, 0.2 part by weight of potassium persulfate was added to the inside of the polymerization apparatus to initiate polymerization reaction, which was continued at 80°C for 15 minutes. The remaining portion (95 wt%) of the emulsified material and 50 parts by weight of 2% aqueous potassium persulfate solution were dropped into the polymerization apparatus over four hours. Further, they were reacted at 80°C for two hours and then were cooled to room temperature (25°C). Finally, 3.5 parts by weight of ammonia water was added to adjust the pH to obtain an aqueous emulsion resin composition of Example 1. The logical Tg of the unsaturated monomer composition in Example 1 was 15°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile

components of 50.3 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 170 mPa·s, pH of 9.0, MFT of 47°C.

[0030]

<Example 2>

The aqueous emulsion resin composition of Example 2 was obtained by the same procedural steps as those in Example 1, except that an emulsified material comprising 258 parts by weight of deionized water, 9.8 parts by weight of ADEKA REASOAP SR-10, 22.5 parts by weight of methyl methacrylate, 300 parts by weight of cyclohexyl methacrylate, 160 parts by weight of 2-ethylhexyl acrylate, 2.5 parts by weight of γ -methacryloxypropyl trimethoxysilane, 10 parts by weight of methacrylic acid, and 5 parts by weight of 2-hydroxyethyl methacrylate was used in place of the emulsified material of Example 1. The logical Tg of the unsaturated monomer composition in Example 2 was 20°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 50.4 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 190 mPa·s, pH of 8.8, MFT of 46°C.

[0031]

<Example 3>

The aqueous emulsion resin composition of Example 3 was obtained by the same procedural steps as those in Example 1, except that an emulsified material comprising 235.5 parts by weight of deionized water, 9.8 parts by weight of ADEKA REASOAP SR-10, 55 parts by weight of methyl methacrylate, 150 parts by weight of cyclohexyl methacrylate, 150 parts by weight of n-butyl methacrylate, 128.5 parts of n-butyl acrylate, 1.5 parts by weight of γ -methacryloxypropyl trimethoxysilane, 12.5 parts by weight of 80% acrylic acid, and 5 parts by weight of diacetone acrylamide was used in place of the emulsified material of Example 1 and after the emulsified material was cooled, a solution of 3.5 parts by weight of ammonia water and 2.6 parts by weight of adipic dihydrazide in 18 parts by weight

of deionized water was added. The logical Tg of the unsaturated monomer composition in Example 3 was 20°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 51.1 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 330 mPa·s, pH of 7.8, MFT of 35°C.

[0032]

<Example 4>

The aqueous emulsion resin composition of Example 4 was obtained by the same procedural steps as those in Example 1, except that AQUARON KH-10 (manufactured by DAI-ICHI KOGYO SEIYAKU CO., LTD) was used in place of ADEKA REASOAP SR-10 in Example 1. The logical Tg of the unsaturated monomer composition in Example 4 was 15°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 50.3 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 150 mPa·s, pH of 8.9, MFT of 48°C.

[0033]

<Comparative example 1>

250 parts by weight of deionized water and 5 parts by weight of EMULGEN 147 (polyoxyethylene lauryl ether, manufactured by KAO Corporation) were fed into a polymerization apparatus equipped with an agitator, a thermometer, and a reflux condenser. After the space within the device was sufficiently filled with nitrogen, the temperature was raised to 75°C. 75 parts by weight of methyltrimethoxysilane (MTMS) and 50 parts by weight of tetraethoxysilane (TEOS) were added, while the temperature in the polymerization apparatus was kept at 75°C and were left for 30 minutes. Further, a mixture of 440 parts by weight of deionized water, 10 parts by weight of AQUARON KH-10, 223 parts by weight of methyl methacrylate, 75 parts by weight of cyclohexyl methacrylate, 190 parts by weight of 2-ethylhexyl acrylate, 2 parts by weight of γ -methacryloxypropyl trimethoxysilane, and 10 parts by weight of methacrylic acid that had been emulsified using a homomixer was prepared. One

portion (5 wt%) of the emulsified material was added to the inside of the polymerization apparatus, while the temperature in the polymerization apparatus was kept at 75°C.

Next, 0.2 part by weight of potassium persulfate was added to the inside of the polymerization apparatus to initiate polymerization reaction, which was continued at 80°C for 15 minutes. Further, the remaining portion (95 wt%) of the emulsified material and 50 parts by weight of 2% aqueous potassium persulfate solution were dropped into the polymerization apparatus over four hours, while the temperature in the polymerization apparatus was kept at 80°C. Further, they were reacted at 80°C for two hours and then were cooled to room temperature (25°C). Finally, 3.5 parts by weight of ammonia water was added to adjust the pH to obtain an aqueous emulsion resin composition of Comparative example 1. The logical Tg of the unsaturated monomer composition in Comparative example 1 was 10°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 41.8 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 60 mPa·s, pH of 5.3, MFT of 38°C.

[0034]

<Comparative example 2>

200 parts by weight of deionized water and 0.2 part by weight of ADEKA REASOAP SR-10 were fed into a polymerization apparatus equipped with an agitator, a thermometer, and a reflux condenser. After the space within the apparatus was sufficiently filled with nitrogen, the temperature was raised to 75°C. A mixture of 260 parts by weight of deionized water, 9.8 parts by weight of ADEKA REASOAP SR-10, 121 parts by weight of methyl methacrylate, 200 parts by weight of cyclohexyl methacrylate, 169 parts by weight of 2-ethylhexyl acrylate, and 10 parts by weight of methacrylic acid that had been emulsified using a homomixer was prepared. One portion (5 wt%) of the emulsified material was added to the inside of the polymerization apparatus, while the temperature in the polymerization apparatus was kept at 75°C.

Next, 0.2 part by weight of potassium persulfate was added to the inside of the polymerization apparatus to initiate polymerization reaction, which was continued at 80°C for 15 minutes. The remaining portion (95 wt%) of the emulsified material and 50 parts by weight of 2% aqueous potassium persulfate solution were dropped into the polymerization apparatus over four hours, while the temperature in the polymerization apparatus was kept at 80°C. Further, they were reacted at 80°C for two hours and then were cooled to room temperature (25°C). Finally, 3.5 parts by weight of ammonia water was added to adjust the pH to obtain an aqueous emulsion resin composition of Comparative example 2. The logical Tg of the unsaturated monomer composition in Comparative example 2 was 15°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 50.2 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 150 mPa·s, pH of 8.9, MFT of 46°C.

[0035]

<Comparative example 3>

The aqueous emulsion resin composition of Comparative example 3 was obtained by the same procedural steps as those in Comparative example 2, except that an emulsified material comprising 260 parts by weight of deionized water, 9.8 parts by weight of ADEKA REASOAP SR-10, 305.5 parts by weight of methyl methacrylate, 183 parts by weight of 2-ethylhexyl acrylate, 1.5 parts by weight of γ -methacryloxypropyl trimethoxysilane, and 10 parts by weight of methacrylic acid was used in place of the emulsified material of Comparative example 2. The logical Tg of the unsaturated monomer composition in Comparative example 3 was 15°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 50.1 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 190 mPa·s, pH of 9.0, MFT of 42°C.

[0036]

<Comparative example 4>

199.4 parts by weight of deionized water and 0.8 part by

weight of NEWREX R-25 (anionic nonreactive surfactant, manufactured by NOF CORPORATION) were fed into a polymerization apparatus equipped with an agitator, a thermometer, and a reflux condenser. After the space within the apparatus was sufficiently filled with nitrogen, the temperature was raised to 75°C. A mixture of 230.6 parts by weight of deionized water, 39.2 parts by weight of NEWREX R-25, 131 parts by weight of methyl methacrylate, 200 parts by weight of cyclohexyl methacrylate, 154 parts by weight of 2-ethylhexyl acrylate, 5 parts by weight of γ -methacryloxypropyl trimethoxysilane, and 10 parts by weight of methacrylic acid that had been emulsified using a homomixer was prepared. One portion (5 wt%) of the emulsified material was added to the inside of the polymerization apparatus, while the temperature in the polymerization apparatus was kept at 75°C.

Next, 0.2 part by weight of potassium persulfate was added to the inside of the polymerization apparatus to initiate polymerization reaction, which was continued at 80°C for 15 minutes. The remaining portion (95 wt%) of the emulsified material and 50 parts by weight of 2% aqueous potassium persulfate solution were dropped into the polymerization apparatus over four hours, while the temperature in the polymerization apparatus was kept at 80°C. Further, they were reacted at 80°C for two hours and then were cooled to room temperature (25°C). Finally, 3.5 parts by weight of ammonia water was added to adjust the pH to obtain an aqueous emulsion resin composition of Comparative example 4. The logical Tg of the unsaturated monomer composition in Comparative example 4 was 20°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 50.2 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 160 mPa·s, pH of 9.2, MFT of 49°C.

[0037]

<Comparative example 5>

The aqueous emulsion resin composition of Comparative example 5 was obtained by the same procedural steps as those

in Comparative example 2, except that an emulsified material comprising 260 parts by weight of deionized water, 9.8 parts by weight of ADEKA REASOAP SR-10, 200 parts by weight of cyclohexyl methacrylate, 285 parts by weight of ethyl acrylate, 5 parts by weight of γ -methacryloxypropyl trimethoxysilane, and 10 parts by weight of methacrylic acid was used in place of the emulsified material of Comparative example 2. The logical T_g of the unsaturated monomer composition in Comparative example 5 was 15°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 49.9 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 160 mPa·s, pH of 8.9, MFT of 28°C.

[0038]

<Comparative example 6>

200 parts by weight of deionized water and 0.2 part by weight of ADEKA REASOAP SR-10 were fed into a polymerization apparatus equipped with an agitator, a thermometer, and a reflux condenser. After the space within the apparatus was sufficiently filled with nitrogen, the temperature was raised to 75°C. A mixture of 285 parts by weight of deionized water, 9.8 parts by weight of ADEKA REASOAP SR-10, 105 parts by weight of methyl methacrylate, 200 parts by weight of cyclohexyl methacrylate, 160 parts by weight of 2-ethylhexyl acrylate, 10 parts by weight of methacrylic acid, and 25 parts by weight of methacryloxypropyl trimethoxysilane that had been emulsified using a homomixer was prepared. One portion (5 wt%) of the emulsified material was added to the inside of the polymerization apparatus, while the temperature in the polymerization apparatus was kept at 75°C.

Next, 0.2 part by weight of potassium persulfate was added to the inside of the polymerization apparatus to initiate polymerization reaction, which was continued at 80°C for 15 minutes. The remaining portion (95 wt%) of the emulsified material and 50 parts by weight of 2% aqueous potassium persulfate solution were dropped into the polymerization apparatus over four hours, while the temperature in the

polymerization apparatus was kept at 80°C. Further, they were reacted at 80°C for two hours and then were cooled to room temperature (25°C). Finally, 3.5 parts by weight of ammonia water was added to adjust the pH to obtain an aqueous emulsion resin composition of Comparative example 6. The logical Tg of the unsaturated monomer composition in Comparative example 6 was 15°C. Properties of the obtained aqueous emulsion resin composition were as follows: nonvolatile components of 50.2 wt%, viscosity (measured using a BM-type viscometer at 60 rpm at 23°C) of 140 mPa·s, pH of 8.9, MFT of higher than 90°C.

[0039]

<Comparative example 7>

The same procedural steps as those in Comparative example 2 were conducted, except that an emulsified material comprising 260 parts by weight of deionized water, 9.8 parts by weight of ADEKA REASOAP SR-10, 12.5 parts by weight of methyl methacrylate, 475 parts by weight of cyclohexyl methacrylate, 2.5 parts by weight of γ -methacryloxypropyl trimethoxysilane, and 10 parts by weight of methacrylic acid was used in place of the emulsified material of Comparative example 2, but coagulation occurred during the reaction to form a gel. The logical Tg of the unsaturated monomer composition in Comparative example 7 was 85°C.

[0040]

Evaluation results on weather resistance, stain resistance, and long-term storage stability of the aqueous emulsion resin compositions obtained in Examples 1 to 4 and Comparative examples 1 to 7 are shown in Tables 1 and 2. The abbreviated term in the tables, i.e., "MMA" means methyl methacrylate, "2EHA" means 2-ethylhexyl acrylate, "MAa" means methacrylic acid, "2HEMA" means 2-hydroxyethyl methacrylate, "nBMA" means n-butyl methacrylate, "nBA" means n-butyl acrylate, "Aa" means acrylic acid, "DAAm" means diacetone acrylamide, "EtA" means ethyl acrylate, "MTMS" means methyltrimethoxysilane, and "TEOS" means tetraethoxysilane.

[0041]

[Table 1]

	Example 1	Example 2	Example 3	Example 4
Component A	1 wt%	0.5 wt%	0.3 wt%	1 wt%
Component B	40 wt%	60 wt%	30 wt%	40 wt%
Component C	MMA 23.6 wt% 2EHA 33.4 wt%	MMA 4.5 wt% 2EHA 32 wt%	MMA 11 wt% nBMA 30 wt% nBA 25.7 wt%	MMA 23.6 wt% 2EHA 33.4 wt%
Other unsaturated monomers	MAa 2 wt%	MAa 2 wt% 2HEMA 1 wt%	Aa 2 wt% DAAm 1 wt%	MAa 2 wt%
Free-radical reactive surfactant	Present	Present	Present	Present
Logical Tg (° C)	15	20	20	15
MFT (° C) before being left	47	46	35	48
Long-term storage stability	○	○	○	○
Weather resistance	○	○	○	○
Stain resistance	○	○	○	○

[0042]

[Table 2]

	Comparative example 1	Comparative example 2	Comparative example 3	Comparative example 4	Comparative example 5	Comparative example 6	Comparative example 7
Component A	0.4 wt%	—	0.3 wt%	1 wt%	1 wt%	5 wt%	0.5 wt%
Component B	15 wt%	40 wt%	—	40 wt%	40 wt%	40 wt%	95 wt%
Component C	MMA 44.6 wt% 2EHA 38 wt%	MMA 24.2 wt% 2EHA 33.8 wt%	MMA 61.1 wt% 2EHA 36.6 wt%	MMA 26.2 wt% 2EHA 30.8 wt%	—	MMA 21 wt% 2EHA 32 wt%	MMA 2.5 wt%
Other unsaturated monomers	MAa 2 wt%	MAa 2 wt%	MAa 2 wt%	MAa 2 wt%	EtA 57wt% MAa 2wt%	MAa 2 wt%	MAa 2 wt%
Free-radical reactive surfactant	Present	Present	Present	Absent	Present	Present	Present
MTMS and TEOS	Present	Absent	Absent	Absent	Absent	Absent	Absent
Logical Tg (° C)	10	15	15	20	15	15	85
MFT (° C) before being left	38	46	42	49	28	Higher than 90	—*2
Long-term storage stability	×	○	○	○	○	—*1	—*2
Weather resistance	○	△	△	△	×	—*1	—*2
Stain resistance	○	△	△	△	×	—*1	—*2

*1: Comparative example 5 was not evaluated because a coating film could not be prepared, due to an MFT of higher than 90° C.

*2: Comparative example 6 was not evaluated because a gel was formed during the reaction.

[0043]

It is shown that coating materials using the aqueous emulsion resin compositions obtained in Examples 1 to 4 were excellent in weather resistance, stain resistance, and long-term storage stability. In contrast, it is shown that Comparative example 1 corresponding to the water dispersion

resin composition described in Patent publication 1 was excellent in weather resistance and stain resistance, but was poor in long-term storage stability. It was indicated that Comparative example 2 was poor in weather resistance and stain resistance because it did not contain component (A). It was indicated that Comparative example 3 was poor in weather resistance and stain resistance because it did not contain component (B). It was indicated that Comparative example 4 was poor in weather resistance and stain resistance because it did not use a free-radical reactive surfactant. It was indicated that Comparative example 5 was poor in weather resistance and stain resistance because it did not contain component (C). Comparative example 6 could not be evaluated because the amount of the contained component (A) was in excess, which resulted in significantly reduced film forming properties. Comparative example 7 could not be evaluated because the amount of the contained component (B) was in excess, which resulted in reduced polymerization stability.

CLAIMS

1. An aqueous emulsion resin composition obtained by emulsion polymerization of an unsaturated monomer composition comprising (A) γ -methacryloxypropyl trimethoxysilane, (B) cyclohexyl methacrylate, and (C) at least one unsaturated monomer selected from the group consisting of methyl methacrylate, butyl (meth)acrylate and 2-ethylhexyl (meth)acrylate in the presence of a free-radical reactive surfactant, wherein the unsaturated monomer composition contains 0.1 to 2 wt% of (A) γ -methacryloxypropyl trimethoxysilane and 25 to 75 wt% of (B) cyclohexyl methacrylate.

2. A coating material containing the aqueous emulsion resin composition according to Claim 1.