

## DESCRIPTION

## Title of Invention

OIL-IN-WATER EMULSION COMPOSITION AND SURFACE  
5 TREATMENT METHOD USING SAME

## Technical Field

[0001]

10 The present invention relates to an oil-in-water type emulsion composition that can be utilized in the fields of coating agents, paints, inks, adhesives, anticorrosives, and fiber treatment agents, and other fields, and to a surface treatment method using the oil-in-water type emulsion composition.

## Background Art

15 [0002]

In recent years, attention has been paid to water-based resin compositions because it is considered to be preferable that resin compositions do not contain organic solvents from the standpoint of resource conservation and environmental protection. Particularly, emulsion compositions containing a synthetic resin are  
20 excellent in drying properties, and therefore it is possible to keep the low viscosity of the emulsion compositions even when the concentration of nonvolatile components is high. Therefore, the emulsion compositions containing a synthetic resin have widely been used in the fields of coating agents, paints, inks, adhesives, anticorrosives, and fiber treatment agents, and other fields.

25 Now, there is a tendency that cured products produced from an emulsion composition of styrene acrylic resins or polyvinyl acetates obtained through an emulsion polymerization method are inferior to cured products of solvent-based resins such as thermosetting resins and ultraviolet ray curable resins in terms of water resistance, acid resistance, and base resistance. Therefore, in order to  
30 solve the problems, a crosslinked type emulsion composition obtained by making use of crosslinking technique and so on has been proposed. Specifically, the crosslinked type emulsion composition for curing at high temperature containing an epoxy (meth)acrylate resin, a polymerizable monomer having a high boiling point, a nonionic emulsifier, an anionic emulsifier (however, only nonreactive  
35 emulsifiers are disclosed for each emulsifier), a curing agent, and water is known

(see, PTL1). However, when the crosslinked type emulsion composition described in PTL1 is used, a step of curing the composition by heat treatment at a high temperature is essential, and the composition cannot be adopted under the situation where high-temperature drying facilities are not available.

5           On the other hand, as the crosslinked type emulsion composition that can be cured at normal temperature, a crosslinked type emulsion composition obtained by mixing an oil-in-water type emulsion composition [A] containing a polyester acrylate resin, a surface active agent, a curing agent, and water and an  
10           oil-in-water type emulsion composition [B] containing a polyester acrylate resin, a curing accelerator, and water is known (see, PTL2).

#### Citation List

##### Patent Literature

[0003]

15           PTL1: JP 05-271366 A  
            PTL2: JP 02-036206 A

#### Summary of Invention

##### Technical Problem

20           [0004]

            According to the studies conducted by the present inventors, it has been proven that a coating film obtained by curing an emulsion composition (hereinafter, referred to as a cured coating film) using a nonreactive surface active agent, such as the crosslinked type emulsion composition described in  
25           PTL2, is insufficient in terms of water resistance, acid resistance, and base resistance in the use under the situation where the coating film makes contact with, for example, rain water, industrial waste water, and so on.

            Thus, the problem to be solved in the present invention is to provide an emulsion composition that can easily be cured at normal temperature and is  
30           capable of achieving a high water resistance, a high acid resistance, and a high base resistance, and to provide a surface treatment method using the emulsion composition.

#### Solution to Problem

35           [0005]

The present inventors have conducted diligent studies to solve the above-described problem to find that the following oil-in-water type emulsion compositions can easily be cured at normal temperature and, with the oil-in-water type emulsion compositions, a cured coating film excellent in water resistance, acid resistance, and base resistance is obtained, and have completed the present invention.

[0006]

That is to say, the present invention relates to the following [1] to [10].

[1] An oil-in-water type emulsion composition comprising:

- 100 parts by mass of a (meth)acrylate-based epoxy resin (A);
- 1 to 200 parts by mass of a polymerizable unsaturated monomer (B);
- 0.1 to 10 parts by mass of a curing accelerator (C);
- 1 to 50 parts by mass of a reactive surface active agent (D); and
- 10 to 200 parts by mass of water (E).

[2] The oil-in-water type emulsion composition according to [1], wherein the reactive surface active agent (D) is at least one selected from the group consisting of ionic reactive surface active agents and nonionic reactive surface active agents.

[3] The oil-in-water type emulsion composition according to [2], wherein the ionic reactive surface active agent is an anionic reactive surface active agent.

[4] The oil-in-water type emulsion composition according to any one of [1] to [3], wherein the polymerizable unsaturated monomer (B) is at least one selected from the group consisting of alkyl (meth)acrylates, alkenyl (meth)acrylates, alkylene glycol di(meth)acrylates, alkoxyalkyl (meth)acrylates, dialkylaminoalkyl (meth)acrylates, acrylonitrile, styrene and derivatives of styrene, and vinyl compounds.

[5] The oil-in-water type emulsion composition according to any one of [1] to [4], wherein the curing accelerator (C) is at least one selected from the group consisting of metal acetyl acetates, metal soaps, vanadium compounds, metal sulfides, and amines.

[6] The oil-in-water type emulsion composition according to any one of [1] to [5], obtained by dropping water (E) into a mixed solution comprising the components (A) to (D) to cause phase-transfer emulsification.

[7] A surface treatment method for a material selected from metals, plastics, concretes, mortar, wood, and glass, the method comprising the steps of: adding a curing agent (F) to the oil-in-water type emulsion composition according to any

one of [1] to [6] to prepare a coating solution; applying the coating solution on the surface of the material; and curing the coating solution at 0 to 50°C to form a cured coating film on the surface of the material.

[8] The surface treatment method according to [7], wherein the curing agent (F) is at least one selected from the group consisting of ketone peroxides, hydroperoxides, and peroxyesters.

[9] The surface treatment method according to [7] or [8], wherein the cured coating film has a film thickness of 0.1 to 2 mm.

[10] The surface treatment method according to any one of [7] to [9], wherein the metal according to [7] comprises at least one selected from the group consisting of iron and aluminum.

#### Advantageous Effects of Invention

[0007]

The oil-in-water type emulsion composition of the present invention can easily be cured at normal temperature and, further, can be utilized even under the situation where high temperature drying facilities are not available, and therefore is industrially advantageous. Moreover, a cured product (a cured coating film) obtained by curing the oil-in-water type emulsion composition of the present invention is excellent in water resistance, acid resistance, and base resistance.

Therefore, the oil-in-water type emulsion composition of the present invention is utilized for the surface treatment of various materials such as metals, plastics, concretes, wood, and glass to impart the effect of improving water resistance, acid resistance, base resistance, and so on to various materials.

#### Description of Embodiments

[0008]

In this specification, a requirement that is considered to be preferable can be selected arbitrarily, and the combination of requirements considered to be preferable can be said to be more preferable.

[Oil-in-water Type Emulsion Composition]

The oil-in-water type emulsion composition of the present invention is an oil-in-water type (O/W type) emulsion composition comprising:

100 parts by mass of a (meth)acrylate-based epoxy resin (A);

1 to 200 parts by mass of a polymerizable unsaturated monomer (B);  
0.1 to 10 parts by mass of a curing accelerator (C);  
1 to 50 parts by mass of a reactive surface active agent (D); and  
10 to 200 parts by mass of water (E).

Hereinafter, explanation will be made on each component in detail.

[0009]

((A): (Meth)acrylate-Based Epoxy Resin)

The (meth)acrylate-based epoxy resin as the component (A) is a resin obtained by reacting an  $\alpha,\beta$ -unsaturated monobasic acid with an epoxy resin having two or more epoxy groups within one molecule. The "(meth)acrylate-based epoxy resin" here denotes all the epoxy resins obtained by reacting an acid having a carbon-carbon double bond between so called  $\alpha,\beta$  positions, such as acrylic acid, methacrylic acid, and crotonic acid with an epoxy compound.

Examples of the epoxy resin having two or more epoxy groups within one molecule include bisphenol type epoxy resins, novolak type epoxy resins, halogenated bisphenol type epoxy resins, halogenated novolak type epoxy resins, cyanurate type epoxy resins, and dimer acid-modified epoxy resins. Among these, bisphenol type epoxy resins, novolak type epoxy resins, and halogenated bisphenol type epoxy resins are preferable. Any of the preferable epoxy resins can be produced by a known method or commercially available products thereof can also be used.

In addition, preferable examples of the "bisphenol type" include bisphenol A type, bisphenol AP type, bisphenol B type, bisphenol BP type, bisphenol C type, bisphenol E type, bisphenol F type, and bisphenol G type, and bisphenol A type is more preferable. Here, bisphenol A denotes 2,2-bis(4-hydroxyphenyl)propane, bisphenol AP denotes 1,1-bis(4-hydroxyphenyl)-1-phenylethane, bisphenol B denotes 2,2-bis(4-hydroxyphenyl)butane, bisphenol BP denotes bis(4-hydroxyphenyl)diphenylmethane, bisphenol C denotes 2,2-bis(3-methyl-4-hydroxyphenyl)propane, bisphenol E denotes 1,1-bis(4-hydroxyphenyl)ethane, bisphenol F denotes bis(4-hydroxyphenyl)methane, and bisphenol G denotes 2,2-bis(4-hydroxy-3-isopropylphenyl)propane.

Moreover, bromination is preferable as "halogenation".

An epoxy resin having at least one epoxy group at each of both ends of the molecule is preferable as the epoxy resin having two or more epoxy groups within one molecule.

The epoxy equivalent of the epoxy resin having two or more epoxy groups within one molecule is preferably 130 to 800 g/eq, more preferably 150 to 600 g/eq, further more preferably 150 to 400 g/eq.

[0010]

Moreover, the  $\alpha,\beta$ -unsaturated monobasic acids include acrylic acid, methacrylic acid, and crotonic acid. Among these, acrylic acid and methacrylic acid are preferable, and methacrylic acid is more preferable.

The reaction of the epoxy resin having two or more epoxy groups within one molecule with the unsaturated monobasic acid is not particularly limited, and a known method can be adopted. Specifically, a method can be adopted in which an epoxy resin having two or more epoxy groups within one molecule and an  $\alpha,\beta$  unsaturated monobasic acid are mixed so that the amount of epoxy group and the amount of carboxy group become almost equivalent, and are reacted preferably under the presence of a stabilizer in an air atmosphere preferably at 80 to 150°C, more preferably 90 to 140°C, further preferably 100 to 140°C until the acid value becomes preferably 30 mgKOH/g or less, more preferably 4 to 25 mgKOH/g, further preferably 6 to 20 mgKOH/g. By adjusting the acid value within the range as mentioned above, the stability of the emulsion becomes favorable and the water resistance can be maintained at a high level.

As the stabilizer, known polymerization inhibitors can be used. Examples of the stabilizer include, but not particularly limited to, hydroquinone compounds such as hydroquinone, methylhydroquinone, trimethylhydroquinone, and *t*-butylhydroquinone; thioether compounds such as phenothiazine, and distearyl thiodipropionate; copper salts such as a copper dialkyl dithiocarbamate (alkyl group is methyl group, ethyl group, propyl group, or butyl group), copper acetate, copper salicylate, cuprous thiocyanate, copper nitrate, copper chloride, copper carbonate, copper hydroxide, and copper acrylate; and manganese salts such as a manganese dialkyl dithiocarbamate (alkyl group is methyl group, ethyl group, propyl group, or butyl group), manganese diphenyl dithiocarbamate, manganese formate, manganese acetate, manganese octanoate, manganese naphthenate, manganese permanganate, and ethylenediaminetetraacetic acid.

[0011]

The (meth)acrylate-based epoxy resin may be modified. Examples of the kind of modification include urethane modification, phenol modification, cresol modification, acid modification, acid anhydride modification, acid pendant

modification, phosphoric acid pendant modification, silicon modification, allyl ether modification, acetoacetylation modification, and partial esterification modification.

The component (A) may be used singly or in combination of two or more.

5 [0012]

((B): Polymerizable Unsaturated Monomer)

The oil-in-water type emulsion composition of the present invention comprises a polymerizable unsaturated monomer as the component (B). In the present specification, the component (A) and the component (B) are sometimes  
10 referred to as "resin components" altogether.

The polymerizable unsaturated monomers as the component (B) include alkyl (meth)acrylates, alkenyl (meth)acrylates, alkylene glycol di(meth)acrylates, alkoxyalkyl (meth)acrylates, dialkylaminoalkyl (meth)acrylates, acrylonitrile, styrene and derivatives of styrene, and vinyl compounds.

15 [0013]

Examples of the alkyl (meth)acrylate include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate, and the number of carbon atoms of the alkyl group is preferably 1 to 10.

Examples of the alkenyl (meth)acrylate include allyl (meth)acrylate, and  
20 the number of carbon atoms of the alkenyl group is preferably 3 to 10, more preferably 3 to 6.

Examples of the alkylene glycol di(meth)acrylate include ethylene glycol di(meth)acrylate, and the number of carbon atoms of the alkylene glycol portion is preferably 2 or 3, more preferably 2.

25 Examples of the alkoxyalkyl (meth)acrylate include methoxyethyl (meth)acrylate, and butoxyethyl(meth)acrylate, and the number of carbon atoms of the alkoxy group is preferably 1 to 10, more preferably 1 to 5, and the number of carbon atoms of the alkyl group is preferably 1 to 5, more preferably 1 to 3.

Examples of the dialkylaminoalkyl (meth)acrylate include  
30 dimethylaminoethyl (meth)acrylate, and diethylaminoethyl (meth)acrylate. The alkyl groups contained in the dialkylamino group may be the same or different from each other, and the number of carbon atoms of the alkyl group is preferably 1 to 10, more preferably 1 to 5, further preferably 1 to 3. Moreover, the number of carbon atoms of the alkyl group that is substituted by the dialkylamino group  
35 and that is bonded to the oxygen atom of the acryloyloxy group is preferably 1 to

5, more preferably 1 to 3.

Examples of the styrene derivatives include  $\alpha$ -methylstyrene, o-divinylbenzene, m-divinylbenzene, and p-divinylbenzene.

5 Examples of the vinyl compound include vinyl esters such as vinyl acetate and vinyl propionate; and halogenated vinyl compounds such as vinylidene chloride.

10 Among these, styrene and derivatives of styrene, and the alkylene glycol di(meth)acrylates are preferable, styrene and ethylene glycol di(meth)acrylate are more preferable, styrene and ethylene glycol dimethacrylate are further preferable, and styrene is particularly preferable.

[0014]

The component (B) has an effect of making the cured coating film formation easy when the oil-in-water type emulsion composition is cured at normal temperature.

15 The component (B) may be used singly or in combination of two or more.

In addition, the oil-in-water type emulsion composition of the present invention can be cured at normal temperature and therefore is advantageous in that even a material having a low boiling point (for example, lower than 200°C, or a material having a boiling point of 180°C or lower, or further a material  
20 having a boiling point of 160°C or lower) can be used as described above.

The content of the component (B) is 1 to 200 parts by mass relative to 100 parts by mass of the component (A). When the content of the component (B) is less than 1 part by mass, it becomes difficult to form the cured coating film in curing the oil-in-water type emulsion composition at normal temperature. On  
25 the other hand, when the content of the component (B) exceeds 200 parts by mass, the mechanical strength of the component (A) is impaired. From the similar standpoint, the content of the component (B) is preferably 5 to 100 parts by mass relative to 100 parts by mass of the component (A), more preferably 10 to 80 parts by mass, further preferably 15 to 60 parts by mass, particularly preferably  
30 20 to 55 parts by mass.

[0015]

((C): Curing Accelerator)

As the curing accelerator that is the component (C), a material that can reduce the curing agent (F), specifically an organic peroxide, added in curing the  
35 oil-in-water type emulsion composition of the present invention at normal

temperature can be used. Specifically, the curing accelerators include, but not particularly limited to, metal acetyl acetates such as copper acetyl acetate, vanadium acetyl acetate, cobalt acetyl acetate, manganese acetyl acetate, and iron acetyl acetate; metal soaps; vanadium compounds such as divanadium pentoxide; metal sulfides such as cobalt sulfide, copper sulfide, manganese sulfide, nickel sulfide, and iron sulfide; and amines including aromatic amines such as N,N-dimethyl aniline and N,N-dimethyl toluidine, trialkylamines such as triethylamine, tripropylamine, and tributylamine, alcoholamines such as monoethanolamine, diethanolamine, and triethanolamine. Among these, metal soaps are preferable.

[0016]

The metal soap here is a salt of a long chain fatty acid such as, for example, stearic acid, lauric acid, ricinoleic acid, octylic acid, and naphthenic acid and a metal (however, metal other than sodium and potassium) such as, for example, lithium, magnesium, calcium, barium, aluminum, zinc, iron, cobalt, manganese, and zirconium. The number of carbon atoms of the long chain fatty acid is preferably 6 to 25, more preferably 6 to 20, further preferably 6 to 15, particularly preferably 7 to 12. The metal is preferably iron, cobalt, and manganese, more preferably cobalt.

The metal soap is preferably iron-containing metal soaps such as iron naphthenate, cobalt-containing metal soaps such as cobalt naphthenate and cobalt octylate, and manganese-containing metal soaps such as manganese octylate, more preferably cobalt-containing metal soaps, further preferably cobalt octylate.

The component (C) may be used singly or in combination of two or more.  
[0017]

The content of the component (C) is 0.1 to 10 parts by mass relative to 100 parts by mass of the component (A). When the content of the component (C) is less than 0.1 parts by mass, curing at normal temperature becomes difficult. On the other hand, even when the content of the component (C) exceeds 10 parts by mass, the effect exhibited by the component (C) hits the ceiling only to increase production costs. From the similar standpoint, the content of the component (C) is preferably 0.3 to 7 parts by mass relative to 100 parts by mass of the component (A), more preferably 0.3 to 5 parts by mass, further preferably 0.3 to 3 parts by mass.

[0018]

((D): Reactive Surface Active Agent)

It is necessary to use a reactive surface active agent as the component (D) in order to suppress the separation of the surface active agent from the resin components and to enhance the water resistance, acid resistance, and base resistance of the cured coating film. With nonreactive surface active agents, the water resistance, acid resistance, and base resistance of the cured coating film become insufficient. The "reactive" here means having radical reactivity, and the reactive surface active agent is preferably a surface active agent having at least one carbon-carbon double bond within the molecule. Conversely, "nonreactive" means not having radical reactivity, and the nonreactive surface active agent is a surface active agent not having a carbon-carbon double bond or the like within the molecule.

The reactive surface active agents (D) include ionic reactive surface active agents and non-ionic (nonionic) reactive surface active agents, and it is preferable to use at least one selected from the group consisting of the ionic and nonionic reactive surface active agents. Either one of the ionic reactive surface active agent and the nonionic reactive surface active agents may be used, but it is more preferable to use both the reactive surface active agents.

Any of anionic reactive surface active agents, cationic reactive surface active agents, and amphoteric reactive surface active agents may be used as the ionic reactive surface active agent, but anionic reactive surface active agents are preferable from the standpoint of easiness of emulsification.

[0019]

Examples of the anionic reactive surface active agent include, but not particularly limited to,  $\alpha$ -sulfo- $\omega$ -(1-alkoxymethyl-2-(2-propenyloxy)ethoxy)-poly(oxy-1,2-ethanediyl) ammonium salts [ADEKA REASOAP (R) SR-10, SR-1025, and so on manufactured by ADEKA CORPORATION],  $\alpha$ -sulfo- $\omega$ -(1-(nonylphenoxy)methyl-2-(2-propenyloxy)ethoxy)-poly(oxy-1,2-ethanediyl) ammonium salts [ADEKA REASOAP (R) SE-10, SE-1025A, and so on manufactured by ADEKA CORPORATION], ammonium polyoxyethylene alkylpropenylphenyl ether sulfates [Aqualon (R) HS-10, HS-5, BC-10, BC-5, and so on manufactured by DKS Co. Ltd.],  $\alpha$ -sulfonato- $\omega$ -[1-(allyloxymethyl)-alkyloxy]polyoxyethylene ammonium salts [Aqualon (R) KH-10 and so on manufactured by DKS Co. Ltd.], ammonium polyoxyalkylene alkenyl ether

sulfates [LATEMUL (R) PD-104 and so on manufactured by Kao Corporation], and alkyl allyl sulfosuccinates [LATEMUL (R) S-180A, S-180, and so on manufactured by Kao Corporation, and ELEMNOL (R) JS-20 manufactured by Sanyo Chemical Industries, Ltd.].

Among these,  $\alpha$ -sulfo- $\omega$ -(1-alkoxymethyl-2-(2-propenyloxy)ethoxy)-poly(oxy-1,2-ethanediyl) ammonium salts [ADEKA REASOAP (R) SR-10, SR-1025, and so on manufactured by ADEKA CORPORATION] are preferable from the standpoint of the water resistance, acid resistance, and base resistance of the cured coating film.

[0020]

Examples of the nonionic reactive surface active agent include, but not particularly limited to,  $\alpha$ -hydro- $\omega$ -(1-alkoxymethyl-2-(2-propenyloxy)ethoxy)-poly(oxy-1,2-ethanediyl) [ADEKA REASOAP (R) ER-10, ER-20, ER-30, and ER-40 manufactured by ADEKA CORPORATION], polyoxyalkylene alkenyl ethers [LATEMUL (R) PD-420, PD-430, and PD-450 manufactured by Kao Corporation], and polyoxyethylene alkylpropenylphenyl ethers [Aqualon (R) RN20, RN30, and RN50 manufactured by DKS Co. Ltd.].

Among these,  $\alpha$ -hydro- $\omega$ -(1-alkoxymethyl-2-(2-propenyloxy)ethoxy)-poly(oxy-1,2-ethanediyl) [ADEKA REASOAP (R) ER-10, ER-20, ER-30, and ER-40 manufactured by ADEKA CORPORATION] are preferable from the standpoint of the water resistance, acid resistance, and base resistance of the cured coating film.

[0021]

Besides, known anionic reactive surface active agents or nonionic reactive surface active agents described in JP 62-104802 A, JP 63-23725 A, JP 63-240931 A, and so on can also be used.

When the ionic reactive surface active agent (anionic reactive surface active agent in particular) and the nonionic reactive surface active agent are used together, the content ratio of the nonionic surface active agent in the component (D) is preferably 80 parts by mass or more, more preferably 90 parts by mass or more.

The content of the component (D) is 1 to 50 parts by mass relative to 100 parts by mass of the component (A). When the content of the component (D) is less than 1 part by mass, the stability of the emulsion is lowered. On the other hand, when the content of the component (D) exceeds 50 parts by mass, it

becomes difficult to form the cured coating film, and the water resistance, acid resistance, and base resistance of the cured coating film are lowered. From the similar standpoint, the content of the component (D) is preferably 5 to 45 parts by mass relative to 100 parts by mass of the component (A), more preferably 10 to 40 parts by mass, further preferably 15 to 35 parts by mass, particularly preferably 15 to 30 parts by mass.

[0022]

In addition, a nonreactive surface active agent may be used together with the reactive surface active agent as the component (D). When the nonreactive surface active agent is used together with the reactive surface active agent, the content of the nonreactive surface active agent is preferably 80 parts by mass or less relative to 100 parts by mass of the component (D), more preferably 50 parts by mass or less, further preferably 30 parts by mass or less, particularly preferably 10 parts by mass or less.

As the nonreactive surface active agent, known anionic surface active agents, cationic surface active agents, amphoteric surface active agents, and nonionic surface active agents that are nonreactive can be used.

Examples of the nonreactive anionic surface active agent include: higher alcohol sulfate such as sodium lauryl sulfate; alkylbenzene sulfonates such as sodium dodecylbenzenesulfonate; alkylnaphthalene sulfonates; potassium alkenylsuccinates; dialkylsulfosuccinates; half-hydrogenated tallow fatty acid salts such as half-hydrogenated tallow fatty acid potassium salts; alkyl diaryl ether disulfonates such as sodium alkyl diphenyl ether disulfonates; sulfuric ester salts of polyoxyalkylene alkyl ethers such as sulfuric ester salts of polyoxyethylene alkyl ethers; sulfuric ester salts of polyoxyalkylene aryl ethers such as sulfuric ester salts of polyoxyethylene alkylphenyl ethers; polyoxyalkylene alkyl ether acetates such as sodium polyoxyethylene lauryl ether acetates; sodium lauroylsarcosine, sodium N-lauroylmethyltaurate, sodium N-cocoylmethyltaurate, and a sodium  $\beta$ -naphthalenesulfonate formalin condensate.

[0023]

Examples of the nonreactive cationic surface active agent include alkyl ammonium salts such as dodecyl ammonium chloride.

Examples of the nonreactive nonionic surface active agents include polyoxyethylene alkyl ethers, polyoxyethylene alkylallyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene

sorbitol fatty acid esters, polyoxyethylene fatty acid esters, polyoxyethylene acyl esters, polyoxyethylene hydrogenated sterols, polyoxyethylene polyoxypropylene alkyl ethers, polyoxyethylene lanolins, polyoxyethylene lanolin alcohols, polyoxyethylene lanolin alcohol ethers, and polyoxyethylene lanolin fatty acid esters.

[0024]

((E): Water)

The oil-in-water type emulsion composition of the present invention comprises 10 to 200 parts by mass of water as the component (E) relative to 100 parts by mass of the component (A). When the content of water is less than 10 parts by mass, it is difficult for the emulsion composition to be of oil-in-water type, and it is also difficult to keep the stability of the emulsion. On the other hand, when the content of water exceeds 200 parts by mass, curing at normal temperature becomes difficult. From the similar standpoint, the content of water is preferably 10 to 150 parts by mass relative to 100 parts by mass of the component (A), more preferably 10 to 100 parts by mass, further preferably 10 to 70 parts by mass, particularly preferably 10 to 50 parts by mass.

As water, purified water such as ion-exchanged water or distilled water is preferable.

In addition, as will be mentioned later, it is preferable that the oil-in-water type emulsion composition of the present invention is an emulsion composition obtained by dropping water (E) into a mixed solution comprising the components (A) to (D) and other components mentioned later as necessary to cause phase-transfer emulsification.

[0025]

(Other Components)

The oil-in-water type emulsion composition of the present invention may comprise, as necessary, various kinds of additives such as a reinforcing material, a filler, and a pigment. Moreover, the oil-in-water type emulsion composition of the present invention may also comprise a water-soluble polymer such as a polyvinyl alcohol, a polyester, polyethylene glycol, and a polyvinyl pyrrolidone. When the water-soluble polymer is contained, the effect of enhancing the stability of the component (A) is obtained.

When the oil-in-water type emulsion composition of the present invention comprises these other components, the content of each of the other components is

preferably 30 parts by mass or less relative to 100 parts by mass of the component (A), more preferably 20 parts by mass or less, further preferably 10 parts by mass or less.

Moreover, when the oil-in-water type emulsion composition of the present invention comprises these other components, the total content of the components (A) to (E) in the oil-in-water type emulsion composition is preferably 50 parts by mass or more, more preferably 70 parts by mass or more, further preferably 80 parts by mass or more, particularly preferably 90 parts by mass or more, more particularly preferably 95 parts by mass or more.

[0026]

#### [Method for Preparing Oil-in-water Type Emulsion Composition]

The method for preparing the oil-in-water type emulsion composition of the present invention is not particularly limited as long as the composition becomes an oil-in-water type emulsion composition. As an example, a method is preferably given in which a mixed solution is obtained by mixing the component (A) to (D) and the other components as necessary, and water is dropped into the mixed solution to cause phase-transfer emulsification. In this case, by "dropping" water, not adding all at once, so called W/O emulsion the continuous phase of which is an oil phase finely changes to so called O/W emulsion the continuous phase of which is water. Moreover, by dropping water, a state is made in which the dispersion phase is more finely dispersed to enhance the stability of the emulsion and also enhance the water resistance, acid resistance and base resistance of the cured coating film.

The rate of dropping water is not particularly limited as long as the rate is not too fast. However, for example, a rate of about 10 to about 300 ml/h is preferable, and a rate of 50 to 150 ml/h is more preferable.

[0027]

#### [Surface Treatment Method]

By conducting surface treatment to various materials such as metals, plastics, concretes, wood, and glass using the oil-in-water type emulsion composition of the present invention, the effect of improving the water resistance, acid resistance, base resistance, and so on of the various kinds of materials can be imparted.

Specifically, a method for forming a cured coating film on the surface of the material by adding the curing agent (F) to the oil-in-water type emulsion

composition of the present invention to prepare a coating solution, then applying the coating solution on the surface of the material, and thereafter curing the coating solution at 0 to 50°C can preferably be utilized.

As the curing agent (F), curing agents generally used for curing  
5 unsaturated polyesters or (meth)acrylate-based epoxy resins can be used. As the curing agent, organic peroxides are preferably used. Specific examples of the organic peroxide include, but not particularly limited to, ketone peroxides such as methyl ethyl ketone peroxide, cyclohexanone peroxide, 3,3,5-trimethylcyclohexanone peroxide, and methylcyclohexanone peroxide;  
10 hydroperoxides such as t-butyl hydroperoxide, cumenhydroperoxide, diisopropylbenzenhydroperoxide, and 2,5-dimethylhexanone-2,5-hydroperoxide; and peroxyesters such as t-butylperoxybenzoate, and t-butylperoxylaurate. As the organic peroxide, an organic peroxide having a 10 hour half-life temperature of 30 to 170°C is preferable. The curing agent may be used singly or in  
15 combination of two or more.

The addition amount of the curing agent (F) is preferably 0.5 to 10 parts by mass relative to 100 parts by mass of the oil-in-water type emulsion composition, more preferably 0.5 to 7 parts by mass, further preferably 1 to 7 parts by mass, particularly preferably 1 to 5 parts by mass. When the addition amount of the  
20 curing agent (F) is 0.5 parts by mass or more relative to 100 parts by mass of the oil-in-water type emulsion composition, a sufficient curing rate and a sufficient hardness are obtained, and the water resistance, acid resistance, and base resistance of the cured coating film become excellent. Moreover, when the addition amount of the curing agent is 10 parts by mass or less, easiness of  
25 coating film formation is not lowered.  
[0028]

The surface treatment method of the present invention is a method that makes it easy to conduct curing at around normal temperature and that can be conducted in an environment where drying facilities are not available, and is an  
30 industrially advantageous surface treatment method. The temperature during curing is preferably 5 to 50°C from the standpoint or the like of the curing rate, more preferably 10 to 50°C, further preferably 15 to 45°C, particularly preferably 15 to 40°C.

The film thickness of the cured coating film that is formed is preferably 0.1  
35 to 2 mm, more preferably 0.3 to 2 mm, further preferably 0.5 to 2 mm,

particularly preferably 0.5 to 1.5 mm from the standpoint of achieving both the desired film thickness being not so large in terms of surface treatment and maintaining the effect of surface treatment for a long period of time. In addition, by adjusting the film thickness of the swollen coating film at the time of coating within these ranges, the film thickness of the cured coating film can be adjusted within the range as described previously.

[0029]

Materials such as metals, plastics, concretes, mortar, wood, and glass are materials that can be used under the situation where these materials make contact with rain water or industrial waste water, and therefore are materials on which the surface treatment using the oil-in-water type emulsion composition of the present invention is desired.

As the metal, a metal comprising at least one selected from the group consisting of iron and aluminum is preferable. These are components contained in the metals that are particularly often used under the situation where the metals make contact with rain water or industrial waste water. As the metal comprising iron, a metal comprising substantially 100% by mass of iron or a metal comprising a metal (such as, for example, chromium) other than iron such as stainless may be used.

The material quality of wood is not particularly limited.

The glass is not particularly limited as long as the glass becomes an amorphous solid that exhibits a glass transition phenomenon by raising the temperature. Glass containing a silicate as a main component may be used, or glass containing a component other than the silicate as a main component, such as acryl glass, chalcogens glass, metal glass, organic glass, or the like, may be used. The surface of the glass to be treated may be flat or may have unevenness formed thereon.

## Examples

[0030]

The present invention will be explained in more detail by Examples, but the present invention is not limited by Examples at all.

[0031]

### Example 1

In a reaction vessel, 948 g of a novolak type epoxy resin "EPICRON (R) N-

740" (epoxy equivalent = 170 to 190 g/eq, manufactured by DIC Corporation), 451 g of methacrylic acid, 1.2 g of hydroquinone, and 6 g of N,N-dimethylbenzylamine were charged and reacted at  $115 \pm 5^\circ\text{C}$  for 2 hours while air was blown into the resultant mixture, and the acid value of a (meth)acrylate-based epoxy resin (A) obtained by the reaction became 10 mgKOH/g. Next, 0.3g of hydroquinone and, as the component (B), 600 g of styrene were added and stirred well to be dissolved. The resin components thus obtained are referred to as resin components (VE-1). In addition, the blending ratio of the component (B) in the resin components is, as shown in Table 1, 30 parts by mass relative to 100 parts by mass of the component (A).

To 100 g of the obtained resin components (VE-1), 1.0 g of cobalt octylate as the component (C), and 1.5 g of an anionic reactive surface active agent "ADEKA REASOAP (R) SR-10" (manufactured by ADEKA CORPORATION) and 25 g of a nonionic reactive surface active agent "ADEKA REASOAP (R) ER-30" (manufactured by ADEKA CORPORATION) as the component (D) were added, and the resultant mixed solution was stirred well while 30 g of water as the component (E) was dropped at 100 ml/h therein to prepare an oil-in-water type emulsion composition 1. In addition, the separation or the like of the surface active agents from the resin components was not observed in the emulsion composition to find that the emulsion was stable.

[0032]

#### Example 2

An oil-in-water type emulsion composition 2 was prepared in the same manner as in Example 1 except that 600 g of ethylene glycol dimethacrylate was used (obtained resin components are referred to as resin components (VE-2)) in place of 600 g of styrene in Example 1. In addition, the separation or the like of the surface active agents from the resin components was not observed in the emulsion composition to find that the emulsion was stable.

[0033]

#### Example 3

In a reaction vessel, 1043 g of a bisphenol A type epoxy resin "Araldite (R) AER-280" (epoxy equivalent = 280 g/eq, manufactured by Asahi Kasei E-materials Corporation), 340 g of methacrylic acid, 0.4 g of hydroquinone, and 3.3 g of N,N-dimethylbenzylamine were charged and reacted at  $125 \pm 5^\circ\text{C}$  for 2 hours while air was blown into the resultant mixture, and the acid value of a

(meth)acrylate-based epoxy resin (A) obtained by the reaction became 10 mgKOH/g. Next, 0.3g of hydroquinone and, as the component (B), 900 g of styrene were added and stirred well to be dissolved. The resin components thus obtained are referred to as resin components (VE-3). In addition, the blending ratio of the component (B) in the resin components is, as shown in Table 1, 45 parts by mass relative to 100 parts by mass of the component (A).

To 100 g of the obtained resin components (VE-3), 1.0 g of cobalt octylate as the component (C), and 1.5 g of an anionic reactive surface active agent "ADEKA REASOAP (R) SR-10" (manufactured by ADEKA CORPORATION) and 25 g of a nonionic reactive surface active agent "ADEKA REASOAP (R) ER-30" (manufactured by ADEKA CORPORATION) as the component (D) were added, and the resultant mixed solution was stirred well while 30 g of water as the component (E) was dropped at 100 ml/h therein to prepare an oil-in-water type emulsion composition 3. In addition, the separation or the like of the surface active agents from the resin components was not observed in the emulsion composition to find that the emulsion was stable.

[0034]

#### Example 4

In a reaction vessel, 948 g of a brominated bisphenol A type epoxy resin "EPICRON (R) 152" (epoxy equivalent = 340 to 380 g/eq, manufactured by DIC Corporation), 451 g of methacrylic acid, 1.2 g of hydroquinone, and 6 g of N,N-diethylamine hydrochloride were charged and reacted at  $125 \pm 5^\circ\text{C}$  for 2 hours while air was blown into the resultant mixture, and the acid value of a (meth)acrylate-based epoxy resin (A) obtained by the reaction became 10 mgKOH/g. Next, 0.3g of hydroquinone and, as the component (B), 500 g of styrene were added and stirred well to be dissolved. The resin components thus obtained are referred to as resin components (VE-4). In addition, the blending ratio of the component (B) in the resin components is, as shown in Table 1, 25 parts by mass relative to 100 parts by mass of the component (A).

To 100 g of the obtained resin components (VE-4), 1.0 g of cobalt octylate as the component (C), and 1.5 g of an anionic reactive surface active agent "ADEKA REASOAP (R) SR-10" (manufactured by ADEKA CORPORATION) and 25 g of a nonionic reactive surface active agent "ADEKA REASOAP (R) ER-30" (manufactured by ADEKA CORPORATION) as the component (D) were added, and the resultant mixed solution was stirred well while 30 g of water as the

component (E) was dropped at 100 ml/h therein to prepare an oil-in-water type emulsion composition 4. In addition, the separation or the like of the surface active agents from the resin components was not observed in the emulsion composition to find that the emulsion was stable.

5 [0035]

#### Comparative Example 1

10 An oil-in-water type emulsion composition 5 was prepared in the same manner as in Example 1 except that styrene in Example 1 was not used (obtained resin component is referred to as a resin component (VE-5)). In addition, the separation or the like of the surface active agents from the resin component was not observed in the emulsion composition to find that the emulsion was stable. [0036] The component (A) and the component (B) used in Examples 1 to 4 and Comparative Example 1, and the blending ratios of the component (A) and the component (B) are shown together in Table 1 below.

15

Table 1

| (unit: g)        |                                           | Examples |      |      |      | Comparative Example |
|------------------|-------------------------------------------|----------|------|------|------|---------------------|
|                  |                                           | 1        | 2    | 3    | 4    | 1                   |
| (A)              | (Meth)acrylate-based epoxy resin (A-1) *1 | 100      | 100  |      |      | 100                 |
|                  | (Meth)acrylate-based epoxy resin (A-3) *2 |          |      | 100  |      |                     |
|                  | (Meth)acrylate-based epoxy resin (A-4) *3 |          |      |      | 100  |                     |
| (B) *4           | Styrene                                   | 30       |      | 45   | 25   |                     |
|                  | Ethylene glycol dimethacrylate            |          | 30   |      |      |                     |
| Resin components |                                           | VE-1     | VE-2 | VE-3 | VE-4 | VE-5                |

\*1: Central skeleton = novolak type epoxy resin

\*2: Central skeleton = bisphenol A type epoxy resin

\*3: Central skeleton = brominated bisphenol A type epoxy resin

\*4: Amount blended (g) relative to 100 g of component (A) is shown.

[0037]

#### Comparative Example 2

20 To 100 g of the resin components (VE-1) obtained in Example 1, 1.0 g of cobalt octylate as the component (C), and 3 g of an anionic reactive surface active agent "ADEKA REASOAP (R) SR-10" (manufactured by ADEKA

CORPORATION) and 65 g of a nonionic reactive surface active agent "ADEKA REASOAP (R) ER-30" (manufactured by ADEKA CORPORATION) as the component (D) were added, and the resultant mixed solution was stirred well while 30 g of water as the component (E) was dropped at 100 ml/h therein to  
5 prepare an oil-in-water type emulsion composition 6. In addition, the separation or the like of the surface active agents from the resin components was not observed in the emulsion composition to find that the emulsion was stable.  
[0038]

### Comparative Example 3

10 An oil-in-water type emulsion composition 7 was prepared in the same manner as in Example 1 except that an anionic nonreactive surface active agent "LATEMUL (R) E-118B" (manufactured by Kao Corporation) was used in place of the anionic reactive surface active agent in Example 1, and that a nonionic  
15 nonreactive surface active agent "EMULGEN (R) 1135-S70" (manufactured by Kao Corporation) was used in place of the nonionic reactive surface active agent in Example 1. In addition, the separation or the like of the surface active agents from the resin components was not observed in the emulsion composition to find that the emulsion was stable.  
[0039]

20 All the components used and the amounts blended in Examples 1 to 4 and Comparative Examples 1 to 3 are shown together in Table 2 below.

Table 2

|                                            |                                           | Examples*5    |               |               |               | Comparative Example*5 |               |               |
|--------------------------------------------|-------------------------------------------|---------------|---------------|---------------|---------------|-----------------------|---------------|---------------|
|                                            |                                           | (unit: g)     | 1             | 2             | 3             | 4                     | 1             | 2             |
| (A)<br>+<br>(B)                            | Resin components (VE-1)                   | 100           |               |               |               |                       | 100           | 100           |
|                                            | Resin components (VE-2)                   |               | 100           |               |               |                       |               |               |
|                                            | Resin components (VE-3)                   |               |               | 100           |               |                       |               |               |
|                                            | Resin components (VE-4)                   |               |               |               | 100           |                       |               |               |
|                                            | Resin components (VE-5)                   |               |               |               |               | 100                   |               |               |
| (C)                                        | Cobalt octylate                           | 1(0.77)       | 1(0.77)       | 1(0.69)       | 1(0.80)       | 1(1.00)               | 1(0.77)       | 1(0.77)       |
| (D)                                        | Anionic reactive surface active agent     | 1.5<br>(1.16) | 1.5<br>(1.16) | 1.5<br>(1.04) | 1.5<br>(1.20) | 1.5<br>(1.50)         | 3.0<br>(2.31) |               |
|                                            | Nonionic reactive surface active agent    | 25<br>(19.3)  | 25<br>(19.3)  | 25<br>(17.3)  | 25<br>(20.0)  | 25<br>(25.0)          | 65<br>(50.0)  |               |
|                                            | Anionic nonreactive surface active agent  |               |               |               |               |                       |               | 1.5<br>(1.16) |
|                                            | Nonionic nonreactive surface active agent |               |               |               |               |                       |               | 25<br>(19.3)  |
| (E)                                        | Water                                     | 30<br>(23.1)  | 30<br>(23.1)  | 30<br>(20.7)  | 30<br>(24.0)  | 30<br>(30.0)          | 30<br>(23.1)  | 30<br>(23.1)  |
| Oil-in-water type emulsion composition No. |                                           | No.1          | No.2          | No.3          | No.4          | No.5                  | No.6          | No.7          |

\*5: Numerical value in parenthesis shows amount blended (g) relative to 100 g of component (A).

[0040]

Examples 5 to 8 and Comparative Examples 4 to 6

Each of the oil-in-water type emulsion compositions obtained in Examples 1 to 4 or Comparative Examples 1 to 3 and a curing agent "328E" (obtained by diluting t-butyl peroxybenzoate and cumenhydroperoxide with a solvent, manufactured by Kayaku Akzo Corporation) were mixed by the amount blended as described in Table 3 to prepare a coating solution, and the coating solution was applied on glass to which a polyester film was stuck so that the wet film thickness became 1 mm. After the application, the glass was left standing in an environment at a temperature of 23°C and a relative humidity of 50% for 3 days to obtain a cured coating film. In addition, the polyester film stuck on the glass

is for preventing the coating film from sticking to the glass.

The easiness of cured coating film formation, and the water resistance, acid resistance, and base resistance of each cured coating film was evaluated following the methods described below. The results are shown in Table 3.

5 [0041]

(Easiness of Cured Coating Film Formation)

10 The state of the coating film when left standing in an environment at a temperature of 23°C and a relative humidity of 50% for 24 hours after the coating solution was applied was evaluated following the evaluation criteria described below.

Excellent: a cured coating film was formed, and the film was not sticky when touched with a finger.

Fair: the coating film was being cured, but the surface of the film was sticky when touched with a finger.

15 Poor: the coating film was not cured.

(Water Resistance, Acid Resistance, and Base Resistance)

20 A test piece obtained by cutting the cured coating film after the cured coating film was left standing for a total of 1 week was immersed in each of water, 10 vol% of sulfuric acid, and saturated calcium hydroxide for 1 week, then the test piece was taken out and washed with ion-exchanged water, and the change in weight was measured to determine, from the following formula 1, the swelling ratio (unit: mass%), which was used as indices of water resistance, acid resistance, and base resistance. The smaller numerical value shows that the water resistance, the acid resistance, or the base resistance is higher.

$$25 \quad \text{Swelling ratio} = \frac{\text{Weight of test piece after immersion} - \text{Weight of test piece before immersion}}{\text{Weight of test piece before immersion}} \times 100 \quad (\text{Formula 1})$$

[0042]

Table 3

|                                            |                                    |                                    | Examples  |           |           |           | Comparative Examples |      |      |
|--------------------------------------------|------------------------------------|------------------------------------|-----------|-----------|-----------|-----------|----------------------|------|------|
|                                            |                                    |                                    | 5         | 6         | 7         | 8         | 4                    | 5    | 6    |
| Oil-in-water type emulsion composition No. |                                    |                                    | No.1      | No.2      | No.3      | No.4      | No.5                 | No.6 | No.7 |
| Amount blended (g)                         |                                    |                                    | 100       | 100       | 100       | 100       | 100                  | 100  | 100  |
| Curing agent (g)                           |                                    |                                    | 3         | 3         | 3         | 3         | 3                    | 3    | 3    |
| Evaluation results                         | Easiness of coating film formation |                                    | Excellent | Excellent | Excellent | Excellent | Poor                 | Fair | Poor |
|                                            | Swelling ratio (mass%)             | Water                              | 2.6       | 3.4       | 4.7       | 4.0       | —*6                  | 10.3 | 5.1  |
|                                            |                                    | Acid (10 vol% sulfuric acid)       | 2.6       | 2.8       | 1.6       | 1.7       | —*6                  | 7.8  | 4.8  |
|                                            |                                    | Base (saturated calcium hydroxide) | 3.2       | 3.0       | 5.0       | 4.3       | —*6                  | 9.6  | 4.5  |

\*6: not evaluated because a cured coating film was not formed even after the coating film was left standing for 1 week.

[0043]

From Table 3, it is understood that the cured coating film formation at normal temperature is easy and the water resistance, acid resistance, and base resistance of the cured coating film are greatly superior in the case where the oil-in-water type emulsion compositions of No. 1 to No. 4 is used when compared in the case where the oil-in-water type emulsion compositions No. 6 or No.7 is used.

Moreover, it is understood that the oil-in-water type emulsion composition No.5 is a composition with which the cured coating film formation is difficult.

Industrial Applicability

[0044]

The oil-in-water type emulsion composition of the present invention can be utilized in the fields of coating agents, paints, inks, adhesives, anticorrosives, and fiber treatment agents, and other fields.

## CLAIMS

[Claim 1]

An oil-in-water type emulsion composition comprising:

100 parts by mass of a (meth)acrylate-based epoxy resin (A);

5 1 to 200 parts by mass of a polymerizable unsaturated monomer (B);

0.1 to 10 parts by mass of a curing accelerator (C);

1 to 50 parts by mass of a reactive surface active agent (D); and

10 to 200 parts by mass of water (E).

[Claim 2]

10 The oil-in-water type emulsion composition according to claim 1, wherein the reactive surface active agent (D) is at least one selected from the group consisting of ionic reactive surface active agents and nonionic reactive surface active agents.

[Claim 3]

15 The oil-in-water type emulsion composition according to claim 2, wherein the ionic reactive surface active agent is an anionic reactive surface active agent.

[Claim 4]

The oil-in-water type emulsion composition according to any one of claims 1 to 3, wherein the polymerizable unsaturated monomer (B) is at least one selected from the group consisting of alkyl (meth)acrylates, alkenyl (meth)acrylates, 20 alkylene glycol di(meth)acrylates, alkoxyalkyl (meth)acrylates, dialkylaminoalkyl (meth)acrylates, acrylonitrile, styrene and derivatives of styrene, and vinyl compounds.

[Claim 5]

25 The oil-in-water type emulsion composition according to any one of claims 1 to 4, wherein the curing accelerator (C) is at least one selected from the group consisting of metal acetyl acetates, metal soaps, vanadium compounds, metal sulfides, and amines.

[Claim 6]

30 The oil-in-water type emulsion composition according to any one of claims 1 to 5, obtained by dropping water (E) into a mixed solution comprising the components (A) to (D) to cause phase-transfer emulsification.

[Claim 7]

35 A surface treatment method for a material selected from the group consisting of metals, plastics, concretes, mortar, wood, and glass, the method

comprising the steps of: adding a curing agent (F) to the oil-in-water type emulsion composition according to any one of claims 1 to 6 to prepare a coating solution; applying the coating solution on the surface of the material; and curing the coating solution at 0 to 50°C to form a cured coating film on the surface of the material.

[Claim 8]

The surface treatment method according to claim 7, wherein the curing agent (F) is at least one selected from the group consisting of ketone peroxides, hydroperoxides, and peroxyesters.

[Claim 9]

The surface treatment method according to claim 7 or 8, wherein the cured coating film has a film thickness of 0.1 to 2 mm.

[Claim 10]

The surface treatment method according to any one of claims 7 to 9, wherein the metal defined in claim 7 comprises at least one selected from the group consisting of iron and aluminum.