

DESCRIPTION

AQUEOUS RESIN COMPOSITION FOR FORMING THICK FILM,
MANUFACTURING METHOD THEREFOR, SURFACE TREATMENT METHOD, AND
A CONCRETE STRUCTURE

TECHNICAL FIELD

[0001] The present invention relates to an aqueous resin composition for forming thick film, a method of producing the aqueous resin composition for forming thick film, a method of surface treatment, and a concrete structure. More specifically, the present invention relates to an aqueous resin composition for forming thick film, the aqueous resin composition for forming thick film being used in surface treatment of a concrete structure that is for use in the field of civil engineering and/or the field of construction, a method of producing the aqueous resin composition for forming thick film, a method of surface treatment, and a concrete structure.

BACKGROUND ART

[0002] Concrete structures degrade under various environmental conditions, and this is a problem. In order to make concrete structures more durable, surface treatment is applied thereto using various resin materials.

The resin materials used in such surface treatment have been affected by increasingly tighter regulations on VOC emissions and by rapidly increasing social awareness of environmental protection, resulting in a shift from organic-solvent-based resin materials to aqueous resin materials. Surface treatment of concrete structures for use in the field of civil engineering and/or the field of construction, in particular, has been receiving increasingly stringent regulations on emission of odor and volatile components, materials, and the like, due to environmental issues and the like. Therefore, development of aqueous resin materials is desired.

[0003] When an aqueous resin material is used in surface treatment of a concrete structure, the aqueous resin material gives a coating that takes a long time to thoroughly dry, in other words, efficiency of the treatment is inadequate. Besides, in terms of durability of the resulting film, an organic-solvent-based resin material, which contains a vinyl ester resin, a polyester resin, an epoxy resin, polyurea, a urethane resin, or the like, is used more commonly because it can form a film superior in water resistance, acid resistance, and alkaline resistance. Thus, the aqueous resin material is not only inadequate in workability, but also inadequate in strength of the resulting film due to less crosslinking sites being formed by the aqueous resin material than by the organic-solvent-based resin material. Therefore, the aqueous resin material is not suitable for use in surface treatment of concrete structures.

[0004] Under such circumstances, an aqueous substrate preparation material for concrete structure is suggested, that contains a polymer emulsion, either an acrylic emulsion or a synthetic rubber emulsion, and talc (see Patent Document 1). This substrate preparation material, however, is limited in the method of application thereof and gives a thick film having inadequate acid resistance and inadequate alkaline resistance.

[0005] A composition for reinforced mortar is also suggested, that contains an emulsion of a copolymer of vinyl acetate with ethylene mixed with glass fiber, cement, sand, and the like (see Patent Document 2). This composition for reinforced mortar, however, has an excess non-volatile content and therefore undergoes a rapid increase in viscosity, presenting a drawback in workability.

[0006] An aqueous resin composition containing a synthetic resin emulsion mixed with an organic filler is also suggested. For example, an adhesive composition containing at least one of a latex of styrene-butadiene copolymer resin and a latex of chloroprene rubber as well as an acrylic resin powder (an organic filler) is suggested (see Patent Document 3). This adhesive composition, however, is intended to be formulated in adhesives, not intended

to give a thick film that is formed, for example, as surface treatment of a concrete structure.

A damping composition is also disclosed, in which a base emulsion containing a core-shell type emulsion is mixed with an organic filler (see Patent Document 4). This damping composition, however, can crack when being formed into a thick film, depending on the drying conditions.

[0007] In order to solve these challenges, the inventors of the present invention developed an aqueous resin composition for forming thick film, the aqueous resin composition for forming thick film containing a synthetic aqueous resin emulsion and an organic filler or a glass filler and having a non-volatile content of 65% to 80% by mass (see Patent Documents 5 and 6). This aqueous resin composition for forming thick film can form a thick film on a surface of a concrete structure or the like, can dry within 12 hours after application, and gives a durable film having water resistance, acid resistance, alkaline resistance, and the like.

REFERENCES

PATENT DOCUMENTS

[0008] Patent Document 1: JP 2009-149767 A

Patent Document 2: JP 2002-179450 A

Patent Document 3: JP 2009-102606 A

Patent Document 4: JP 2005-126645 A

Patent Document 5: JP 2011-256289 A

Patent Document 6: JP 2011-57802 A

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009] In the surface treatment of concrete structures, there are demands to withstand increasingly stringent environments. For example, in the concrete structures which used in many wastewater treatment facilities, since the

facilities are covered, the concrete structures are seriously corroded by generating sulfuric acid. Against this backdrop, materials used in surface treatment of concrete structures must meet the quality standards C and D defined in "Technical Manual on Corrosion Prevention and Corrosion Protection for Concrete Sewage Structures" (April 2012) issued by the general incorporated foundation Sewerage Business Management Centre.

The aqueous resin composition for forming thick film in Patent Documents 5 and 6 developed by the inventors of the present invention is good enough to form a film excellent in water resistance, acid resistance, and alkaline resistance, but it fails to meet the quality standards C and D.

[0010] The present invention has been devised to solve this problem. Objects of the present invention are to provide an aqueous resin composition for forming thick film, in which the aqueous resin composition for forming thick film can form a thick film and can dry within 12 hours after application, produces no odor during application, can form a film excellent in water resistance, acid resistance, and alkaline resistance, and, in particular, can form a film that meets the quality standards C and D defined in "Technical Manual on Corrosion Prevention and Corrosion Protection for Concrete Sewage Structures" (April 2012), and to provide a method of producing the aqueous resin composition for forming thick film, a method of surface treatment, and a concrete structure.

MEANS FOR SOLVING THE PROBLEMS

[0011] The inventors of the present invention have conducted intensive research to achieve these objects. As a result, the inventors of the present invention have found that by using an aqueous resin composition for forming thick film, the aqueous resin composition for forming thick film comprising a synthetic aqueous resin emulsion and a filler and having a non-volatile content of 65% to 80% by mass, and subjecting the aqueous resin composition for forming thick film to vacuum degassing treatment so as to control the ratio of the observed specific gravity to the theoretical specific gravity to be 97% or

more, the resulting film can meet the quality standards C and D, to thus complete the present invention.

The present invention is characterized by the following items (1) to (8).

[0012] (1) An aqueous resin composition for forming thick film, comprising a synthetic aqueous resin emulsion (A) and a filler (B), having a non-volatile content of 65% to 80% by mass, and having a ratio of an observed specific gravity to a theoretical specific gravity of 97% or more.

(2) The aqueous resin composition for forming thick film according to item (1), having received vacuum degassing treatment.

(3) The aqueous resin composition for forming thick film according to item (1) or (2), wherein the synthetic aqueous resin emulsion (A) is a styrene-acrylate resin emulsion.

(4) The aqueous resin composition for forming thick film according to any one of items (1) to (3), wherein the filler (B) is at least one kind selected from the group consisting of polystyrene, polyethylene, polypropylene, glass frit, glass flake, talc, and clay.

[0013] (5) A method of producing an aqueous resin composition for forming thick film, the aqueous resin composition for forming thick film comprising a synthetic aqueous resin emulsion (A) and a filler (B), having a non-volatile content of 65% to 80% by mass, and having a ratio of observed specific gravity to theoretical specific gravity of 97% or more,

the method comprising:

mixing the synthetic aqueous resin emulsion (A) and the filler (B), and then carrying out vacuum degassing treatment.

(6) A method of surface treatment, comprising:

applying the aqueous resin composition for forming thick film according to any one of items (1) to (4) to a surface of a subject to be surface-treated and

then performing drying to form a film.

(7) The method of surface treatment according to item (6), wherein the subject to be surface-treated is a concrete structure.

(8) A concrete structure having a protective film on a surface thereof, wherein

the protective film is obtained by applying the aqueous resin composition for forming thick film according to any one of items (1) to (4) to a surface of a subject to be surface-treated and then performing drying.

EFFECTS OF THE INVENTION

[0014] The present invention can provide an aqueous resin composition for forming thick film, in which the aqueous resin composition for forming thick film can form a thick film and can dry within 12 hours after application, produces no odor during application, can form a film excellent in water resistance, acid resistance, and alkaline resistance, and, in particular, can form a film that meets the quality standards C and D defined in "Technical Manual on Corrosion Prevention and Corrosion Protection for Concrete Sewage Structures" (April 2012). The present invention can also provide a method of producing the aqueous resin composition for forming thick film, a method of surface treatment, and a concrete structure.

BEST MODE FOR CARRYING OUT THE INVENTION

[0015] The present invention will be described in detail.

The aqueous resin composition for forming thick film of the present invention comprises a synthetic aqueous resin emulsion (A) and a filler (B).

The synthetic aqueous resin emulsion (A) is a polymer emulsion or a polymer latex that can be obtained by using a water-soluble polymer, a surfactant, or the like and carrying out radical polymerization of a composition or the like that contains an unsaturated ethylene monomer.

Examples of the polymer emulsion include a styrene-acrylate resin emulsion, an acrylic resin emulsion, an ethylene-vinyl acetate emulsion, a vinyl

acetate emulsion, a urethane emulsion, a urethane-acrylate emulsion, a polyester emulsion, and a polyester-acrylate emulsion. Examples of the polymer latex include a latex of a styrene-butadiene resin, a latex of an acrylonitrile-butadiene resin, and a latex of a chloroprene resin. These can be used alone or as a combination of two or more of these. In addition to the polymer emulsion or the polymer latex, a suspension of an organic resin emulsified or dispersed in water can be concurrently used.

Among these various components, from the viewpoint of regulation of the non-volatile content and other properties of the synthetic aqueous resin emulsion (A), designing of Tg of the resin or the resins, miscibility, and physical properties, a styrene-acrylate resin emulsion and an acrylic resin emulsion are preferable. In terms of excellent acid resistance and excellent alkaline resistance, a styrene-acrylate resin emulsion is particularly preferable.

[0016] The styrene-acrylate resin emulsion can be obtained by carrying out radical polymerization of a composition or the like that contains an unsaturated ethylene monomer, in the presence of a water-soluble or water-dispersible polyester.

The styrene-acrylate resin emulsion contains a component attributable to a styrene monomer, at a ratio of preferably from 10% to 80% by mass and more preferably from 40% to 60% by mass relative to the sum of the resin components. When the ratio of the component attributable to a styrene monomer is lower than 10% by mass, the film may have low toughness. When the ratio of the component attributable to a styrene monomer exceeds 80% by mass, film formation properties may be impaired and the film may have impaired physical properties. In order to enhance film formation properties, the amount of a film-forming aid may need to be increased.

[0017] The filler (B) is not particularly limited and can be an organic filler, an inorganic filler, or a mixture thereof.

The organic filler is not particularly limited, but is preferably a powder of an organic polymer that is sparingly soluble in water. Being sparingly soluble in

water, herein, means that the solubility in 100 g of water at 23°C and 1 atm is 0.1 g or lower.

The organic filler is not particularly limited and can be, for example, a thermoplastic resin powder (low profile additive) added for purposes such as prevention of cracking or warping of an article that is formed of an unsaturated polyester resin. Examples of the organic filler include polyethylene, polypropylene, polystyrene, polymethyl methacrylate, and a copolymer thereof, vinyl acetate and a copolymer thereof, an unsaturated polyester (an aliphatic ester, an aromatic ester), cellulose acetate butyrate, an ϵ -caprolactone polymer, polybutadiene, and polyvinyl chloride. An elastomer polymer such as styrene-butadiene-styrene (SBS) block polymer, starch powder, and cellulose powder may also be used. These can be used alone or as a mixture of two or more thereof. Among these components, from the viewpoints of miscibility and durability, polystyrene, polyethylene, and polypropylene are preferable and polystyrene is particularly preferable.

[0018] The inorganic filler is not particularly limited. Examples thereof include glass frit, glass flake, glass bead, glass fiber, quartz sand, talc, mica, clays such as kaolin clay and calcined clay, aluminum hydroxide, zinc oxide, titanium oxide, silicic acid, silicates, magnesium oxide, and silica. These can be used alone or as a mixture of two or more of these. Among these components, from the viewpoints of miscibility and durability, glass frit, glass flake, talc, and clays are particularly preferable.

[0019] The content of the filler (B) is not particularly limited, but is preferably 15% by mass or more, more preferably 20% by mass or more, further preferably 25% by mass or more, and most preferably 30% by mass or more relative to the non-volatile content of the aqueous resin composition for forming thick film. When the content of the filler (B) is lower than 15% by mass relative to the non-volatile content of the aqueous resin composition for forming thick film, not only drying properties but also water-sealing properties, acid resistance, and alkaline resistance of the resulting thick film tend to decline.

The upper limit to the content of the filler (B) is not particularly limited, but is preferably 85% by mass or less, more preferably 80% by mass or less, further preferably 75% by mass or less, and most preferably 70% by mass or less relative to the non-volatile content of the aqueous resin composition for forming thick film.

[0020] The average particle diameter of the filler (B) is not particularly limited. However, from the viewpoint of dispersibility, the average particle diameter of the filler (B) is from 1 μm to 150 μm , preferably from 1 μm to 100 μm , and more preferably from 1 μm to 50 μm . In the present specification, the “average particle diameter” refers to an average particle diameter measured, for example, by the laser diffraction/scattering method or the Coulter counter method. The average particle diameter is preferably measured by the laser diffraction/scattering method. The average particle diameter measured, for example, by the laser diffraction/scattering method or the Coulter counter method refers to the average particle diameter of cumulative 50% particles in the particle size distribution measured by such a method. When the average particle diameter of the filler (B) is smaller than 1 μm , the filler (B) readily aggregates and may not give desired dispersibility. When the average particle diameter of the filler (B) exceeds 150 μm , uniform dispersion of the filler (B) in the aqueous resin composition for forming thick film is difficult to achieve, uniform film is also difficult to be formed, and physical properties of the film (strength, durability) may be impaired.

[0021] In the aqueous resin composition for forming thick film of the present invention, the ratio (mass ratio) of the solid matter (non-volatile component) of the synthetic aqueous resin emulsion (A) to the solid matter of the filler (B) is not particularly limited, but is preferably from 8/2 to 2/8, more preferably from 7/3 to 3/7, and most preferably from 6/4 to 4/6. In the present specification, the solid matters of the synthetic aqueous resin emulsion (A) and the filler (B) refer to non-volatile components that do not volatilize during film formation and remain in the film. When the ratio of the solid matter of the synthetic aqueous

resin emulsion (A) to the solid matter of the filler (B) (hereinafter, called "solid matter ratio") exceeds 8/2, in other words, when the synthetic aqueous resin emulsion (A) contains excess solid matter, desired drying properties may not be obtained and physical properties of the film (for example, strength and durability) may be impaired. When the solid matter ratio is lower than 2/8, in other words, when the filler (B) contains excess solid matter, not only does the aqueous resin composition for forming thick film have inadequate stability, but uniform film is also difficult to form, and as a result, durability (water resistance, acid resistance, alkaline resistance) of the film may decline.

[0022] The aqueous resin composition for forming thick film of the present invention can contain a well-known plasticizer, a well-known tackifier resin, a well-known thickener, a well-known curing agent, a well-known defoaming agent, a well-known preservative, and the like added as needed in accordance with an intended use, provided that the effects of the present invention are not impaired.

[0023] The aqueous resin composition for forming thick film of the present invention can be prepared by mixing the components described above and then carrying out vacuum degassing treatment. In the present specification, the "vacuum degassing treatment" refers to mixing in a mixing apparatus under reduced pressure that is being created with a vacuum pump or the like. The mixing apparatus is not particularly limited, and can be a dissolver, a Banbury (trademark) mixer, a planetary mixer, a grain mixer, an open kneader, or a vacuum kneader, for example.

[0024] The aqueous resin composition for forming thick film of the present invention has a ratio of observed specific gravity to theoretical specific gravity of 97% or more. Theoretical specific gravity herein refers to the theoretical value of specific gravity determined from the specific gravity of each component contained in the aqueous resin composition for forming thick film. Observed specific gravity herein refers to a measured value of specific gravity of the

aqueous resin composition for forming thick film that is actually prepared. The specific gravity values can be measured by the gravimetric method.

The method of controlling the ratio of the observed specific gravity to the theoretical specific gravity to be 97% or more is not particularly limited. The control can be achieved by carrying out the vacuum degassing treatment described above. When the ratio of the observed specific gravity to the theoretical specific gravity is controlled to be 97% or more, the resulting film can be remarkably enhanced in its acid resistance and can meet the quality standards C and D defined in "Technical Manual on Corrosion Prevention and Corrosion Protection for Concrete Sewage Structures" (April 2012). In order to control the ratio of the observed specific gravity to the theoretical specific gravity to be 97% or more, a considerable amount (generally, not less than 10 times the usual amount) of a defoaming agent is generally required. The vacuum degassing treatment eliminates the need for increasing the amount of a defoaming agent to be added.

[0025] The minimum film-forming temperature of the aqueous resin composition for forming thick film of the present invention is not particularly limited, but is preferably from 0°C to 5°C and more preferably 0°C. When the minimum film-forming temperature is higher than 5°C, the film is readily affected by drying-temperature conditions, and, as a result, film formation properties may be impaired and a film having desired durability may not be obtained. The method of controlling the minimum film-forming temperature of the aqueous resin composition for forming thick film is not particularly limited. The control can be achieved by addition of a film-forming aid, or by addition of a synthetic aqueous resin emulsion (A) having a relatively low minimum film-forming temperature to a synthetic aqueous resin emulsion (A) having a relatively high minimum film-forming temperature.

[0026] The aqueous resin composition for forming thick film of the present invention has a non-volatile content from 65% to 80% by mass and preferably from 65% to 75% by mass. When the non-volatile content is regulated to this

range, excellent drying properties can be obtained. When the non-volatile content is lower than 65% by mass, drying properties to be obtained are inadequate and addition of considerable amounts of additives is required for adequate workability. When the non-volatile content exceeds 80% by mass, the aqueous resin composition for forming thick film has impaired stability and consequently undergoes a rapid increase in viscosity, presenting a drawback in workability. The non-volatile content is not particularly limited in the method of measuring the same, and can be measured by a method that is known in the technical field to which the present invention pertains. The non-volatile content, however, is preferably measured by a method described in the Example section.

[0027] The viscosity of the aqueous resin composition for forming thick film of the present invention is not particularly limited, but is preferably from 8,000 mPa·s to 80,000 mPa·s, more preferably from 9,000 mPa·s to 60,000 mPa·s, and most preferably from 10,000 mPa·s to 50,000 mPa·s. When the viscosity is regulated to this range, a film as thick as 1 mm or more can be obtained. A viscosity lower than 8,000 mPa·s may cause dripping after application and may cause defects such as cracks during drying. A viscosity exceeding 80,000 mPa·s impairs workability and is, therefore, usually impractical in the applications of the present invention. The method of measuring the viscosity is not particularly limited, and the viscosity can be measured by a method that is known in the technical field to which the present invention pertains. The viscosity, however, is preferably measured by a method described in the Examples section.

[0028] When the aqueous resin composition for forming thick film of the present invention is applied to a surface of a subject to be surface-treated and then dried, the resulting film has a film thickness of preferably from 0.1 mm to 2 mm and more preferably from 0.5 mm to 2 mm. The method of measuring the film thickness is not particularly limited, and the film thickness can be measured with a commercially available film thickness meter. When the film thickness is smaller than 0.1 mm, the film may have pinholes or the like and

therefore may not be adequately continuous, depending on the surface state of the subject to be surface-treated. When the film thickness exceeds 2 mm, the film takes a long time to dry, which may result in inadequate performance to be exhibited by the film.

[0029] The aqueous resin composition for forming thick film of the present invention contains no organic solvent or the like or contains only a small amount of an organic solvent or the like. As a result, the aqueous resin composition for forming thick film of the present invention produces no odors during application, is environmentally friendly, and has excellent drying properties. In addition, when the aqueous resin composition for forming thick film of the present invention is applied to a surface of a concrete structure or another subject to be surface-treated and then air-dried at normal temperature, a film excellent in water resistance, acid resistance, and alkaline resistance can be obtained. The resulting film is expected to function as a protective film and eventually improve durability of the surface of the subject to be surface-treated. The concrete structure herein includes a normal structure made of concrete, mortar, or the like.

[0030] The method of application of the aqueous resin composition for forming thick film of the present invention is not particularly limited. Examples of the method include spray coating, roller coating, and troweling. The amount (solid matter) to apply is simply required to be determined as appropriate in accordance with an intended use, and is preferably from 0.1 kg/m² to 3.0 kg/m² and more preferably from 0.5 kg/m² to 2.5 kg/m². When the amount to apply is smaller than 0.1 kg/m², the resulting film may not be adequately continuous and may have pinholes or the like. When the amount to apply exceeds 3.0 kg/m², the film takes a long time to dry, which may result in inadequate performance to be exhibited by the film.

[0031] When the aqueous resin composition for forming thick film of the present invention is applied to a surface of a concrete structure or another subject to be surface-treated, a primer paint can also be used. Examples of the

primer paint include an acrylic-emulsion-based primer paint (primer, sealer), an epoxy-based primer paint, and a urethane-based primer paint.

EXAMPLES

[0032] The present invention will be described in detail referring to examples and comparative examples. The scope of the present invention, however, is not limited to these examples and comparative examples. Various properties of a synthetic aqueous resin emulsion used in the examples and the comparative examples as well as various properties of an aqueous resin composition for forming thick film prepared in the examples and the comparative examples were evaluated by the following methods.

[0033] (Non-volatile content)

About 1 g of a synthetic aqueous resin emulsion was put and weighed on an aluminum dish having a diameter of 5 cm, and was then dried at 105°C for 1 hour. The residue was weighed, and the resulting weight was used as the non-volatile content.

(Viscosity)

Measurement was carried out with a Brookfield rotational viscometer, at a fluid temperature of 23°C and a rotational speed of 10 rpm, and with a No.5 rotor.

(pH)

Measurement of pH of an aqueous resin composition for forming thick film was carried out with a pH meter.

(Minimum film-forming temperature (MFT))

The MFT of an aqueous resin composition for forming thick film was measured in accordance with JIS K 6828.

[0034] (Drying properties)

A frame was formed on a glass plate, and the frame was filled with an aqueous resin composition for forming thick film that was poured in such a way that the film thickness after drying became 2 mm. The time to dry the

surface in an environment of 20°C × 50%RH to the extent that a finger left no mark on the surface was noted.

(Cracks)

After drying in the evaluation of the drying properties, visual observation for cracks was performed.

○: No cracks observed

△: Wrinkles or the like observed on the surface of the film (change in appearance in the drying step was observed)

× : Cracks observed

[0035] (Ratio of observed specific gravity to theoretical specific gravity)

The ratio of observed specific gravity to theoretical specific gravity was determined by calculating: (observed specific gravity)/(theoretical specific gravity) × 100.

The observed specific gravity of an aqueous resin composition for forming thick film was measured by placing the aqueous resin composition for forming thick film in a container having a certain capacity and employing the gravimetric method.

The theoretical specific gravity of an aqueous resin composition for forming thick film was calculated by determining the volumes of the following components based on the specific gravity values thereof at 23°C and the contents thereof, and then performing calculation by Formula (1) below.

- Emulsion (a copolymer of styrene with acrylic acid ester, non-volatile content: 50% by mass, ratio of a styrene-attributable component relative to the sum of the resin components: 50% by mass, ratio of a component attributable to an acrylic acid ester relative to the sum of the resin components: 50% by mass, viscosity: 4500 mPa·s, minimum film-forming temperature: 0°C): 1.06 mg/mL

- Polystyrene resin powder (SGP-70C): 1.05 mg/mL

- Glass filler (CF0007-05B): 2.6 mg/mL

- Talc (PKP-80): 2.8 mg/mL

- Defoaming agent (Nopco 8034L): 0.92 mg/mL

Theoretical specific gravity (mg/mL) = (total weight of constituents (mg))/(total volume of constituents (mL)) (1)

[0036] (Example 1)

As a synthetic aqueous resin emulsion (A), an emulsion (a copolymer of styrene with acrylic acid ester, non-volatile content: 50% by mass, ratio of a styrene-attributable component relative to the sum of the resin components: 50% by mass, ratio of a component attributable to an acrylic acid ester relative to the sum of the resin components: 50% by mass, viscosity: 4500 mPa·s, minimum film-forming temperature: 0°C) was used. As a filler (B), a polystyrene resin powder (SGP-70C, manufactured by Soken Chemical & Engineering Co., Ltd., average particle diameter: 19 μm) was used.

To 100 parts by mass of the emulsion, 50 parts by mass of the polystyrene resin powder and then 0.05 part by mass of a defoaming agent (Nopco 8034L: manufactured by San Nopco Limited) were added. The resultant mixture was mixed and stirred in a planetary mixer (manufactured by PRIMIX Corporation, T.K. HIVIS DISPER MIX Model 3D-5) at 45 rpm for 5 minutes. Subsequently, an oil rotary vacuum pump was used to reduce pressure so that the gauge pressure became -0.09 MPaG, followed by mixing and stirring for another 10 minutes to give an aqueous resin composition for forming thick film. The resulting aqueous resin composition for forming thick film was filtrated through an 80-mesh filter cloth, and as a result, no coarse particles or aggregates were confirmed.

[0037] (Example 2)

An aqueous resin composition for forming thick film was obtained with the use of the same emulsion as in Example 1 and in the same manner as in Example 1 except that a glass filler (CF0007-05B, manufactured by Nippon Frit Co., Ltd., average particle diameter: 15 μm) was used as a filler. The resulting aqueous resin composition for forming thick film was filtrated through an 80-

mesh filter cloth, and as a result, no coarse particles or aggregates were confirmed.

[0038] (Example 3)

An aqueous resin composition for forming thick film was obtained with the use of the same synthetic aqueous resin emulsion (A) as in Example 1 and in the same manner as in Example 1 except that a polystyrene resin powder (SGP-70C, manufactured by Soken Chemical & Engineering Co., Ltd., average particle diameter: 19 μm) and a glass filler (CF0007-05B, manufactured by Nippon Frit Co., Ltd., average particle diameter: 15 μm) were used as a filler (B). The amount of each of the polystyrene resin powder and the glass filler was 25 parts by mass relative to 100 parts by mass of the emulsion. The resulting aqueous resin composition for forming thick film was filtrated through an 80-mesh filter cloth, and, as a result, no coarse particles or aggregates were confirmed.

[0039] (Example 4)

An aqueous resin composition for forming thick film was obtained with the use of the same synthetic aqueous resin emulsion (A) as in Example 1 and in the same manner as in Example 1 except that a polystyrene resin powder (SGP-70C, manufactured by Soken Chemical & Engineering Co., Ltd., average particle diameter: 19 μm) and talc (PKP-80, manufactured by Fuji Talc, average particle diameter: 13 μm) were used as a filler (B). The amount of each of the polystyrene resin powder and the PKP-80 was 25 parts by mass relative to 100 parts by mass of the emulsion. The resulting aqueous resin composition for forming thick film was filtrated through an 80-mesh filter cloth, and, as a result, no coarse particles or aggregates were confirmed.

[0040] (Comparative Example 1)

The same materials as in Example 1 were used.

To 100 parts by mass of a synthetic aqueous resin emulsion (A), 50 parts by mass of a polystyrene resin powder and then 0.05 part by mass of a defoaming agent (Nopco 8034L: manufactured by San Nopco Limited) were

added. The resultant mixture was mixed and stirred in a disperser at 3000 rpm for 10 minutes to give an aqueous resin composition for forming thick film. The resulting aqueous resin composition for forming thick film was filtrated through an 80-mesh filter cloth, and, as a result, no coarse particles or aggregates were confirmed.

[0041] (Comparative Example 2)

An aqueous resin composition for forming thick film was obtained in the same manner as in Comparative Example 1 except that a glass filler (CF0007-05B, manufactured by Nippon Frit Co., Ltd., average particle diameter: 15 μm) was used as a filler (B). The resulting aqueous resin composition for forming thick film was filtrated through an 80-mesh filter cloth, and as a result, no coarse particles or aggregates were confirmed.

[0042] (Comparative Example 3)

An aqueous resin composition for forming thick film was obtained in the same manner as in Comparative Example 1 except that a polystyrene resin powder (SGP-70C, manufactured by Soken Chemical & Engineering Co., Ltd., average particle diameter: 19 μm) and a glass filler (CF0007-05B, manufactured by Nippon Frit Co., Ltd., average particle diameter: 15 μm) were used as a filler (B). The amount of the polystyrene resin powder and the glass filler were each 25 parts by mass relative to 100 parts by mass of the synthetic aqueous resin emulsion (A). The resulting aqueous resin composition for forming thick film was filtrated through an 80-mesh filter cloth, and, as a result, no coarse particles or aggregates were confirmed.

[0043] (Comparative Example 4)

An aqueous resin composition for forming thick film was obtained in the same manner as in Comparative Example 3 except that the amount of the defoaming agent was changed to 0.25 part by mass. The resulting aqueous resin composition for forming thick film was filtrated through an 80-mesh filter cloth, and, as a result, no coarse particles or aggregates were confirmed.

[0044] (Comparative Example 5)

An aqueous resin composition for forming thick film was obtained in the same manner as in Comparative Example 3 except that the amount of the defoaming agent was changed to 0.50 part by mass. The resulting aqueous resin composition for forming thick film was filtrated through an 80-mesh filter cloth, and as a result, no coarse particles or aggregates were confirmed.

[0045] The composition and various properties of each aqueous resin composition for forming thick film prepared in the examples and the comparative examples are shown in Table 1.

[0046]

	Examples				Comparative Examples				
	1	2	3	4	1	2	3	4	5
Emulsion	100	100	100	100	100	100	100	100	100
Polystyrene resin powder	50	--	25	25	50	--	25	25	25
Glass filler	--	50	25	--	--	50	25	25	25
Talc	--	--	--	25	--	--	--	--	--
Defoaming agent	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.25	0.50
Non-volatile content (% by mass)	66.7	66.7	66.7	66.7	66.7	66.7	66.7	66.7	66.7
Viscosity (mPa×s)	15,000	12,000	16,000	24,000	16,000	19,000	21,000	19,000	18,000
pH	7	7	7	7	7	7	7	7	7
Duration of vacuum degassing treatment (minute)	10	10	10	10	--	--	--	--	--
Observed specific gravity (mg/mL)	1.04	1.30	1.18	1.18	1.01	1.22	1.12	1.13	1.14
Theoretical specific gravity (mg/mL)	1.06	1.33	1.20	1.19	1.06	1.33	1.20	1.20	1.20
Ratio of observed specific gravity to theoretical specific gravity (%)	98.1	97.7	98.3	99.2	95.3	91.7	93.3	94.2	95.0
MFT (°C)	0	0	0	0	0	0	0	0	0
Drying properties	Within 12h	Within 12h	Within 12h	Within 12h	Within 12h	Within 12h	Within 12h	Within 12h	Within 12h
Cracks	○	○	○	○	○	○	○	○	○

[0047] As shown in Table 1, each aqueous resin composition for forming thick film prepared in Examples 1 to 4 as well as each aqueous resin composition for forming thick film prepared in Comparative Examples 1 to 5 had excellent drying properties, and had no cracks when formed into a thick film.

[0048] Each aqueous resin composition for forming thick film prepared in the examples and the comparative examples was poured into a frame that was formed on a glass plate having a release film attached thereto, in such a way that the film thickness became 2 mm (amount applied (solid matter): 2.5 kg/m²). After drying at normal temperature for 4 days, the resulting film was removed from the glass plate, flipped upside down, and then dried this time on the other side at normal temperature for 3 days, whereby a film was prepared.

The film thus prepared was evaluated as follows.

[0049] (Coefficient of film swelling)

From the film prepared above, a fragment of 40 mm × 40 mm was cut out, and the mass of the fragment was measured, which was the pre-immersion film mass of the film. Subsequently, the film was immersed in a 10% aqueous sulfuric acid solution at 40°C for 7 days, and was then taken out. The mass of the film was measured again, which was the after-immersion film mass of the film. These mass values were substituted into the following formula to calculate the coefficient of film swelling. The coefficient of film swelling is preferably not higher than 10% from the viewpoint of acid resistance.

Coefficient of film swelling = ((after-immersion film mass) - (pre-immersion film mass))/(pre-immersion film mass) × 100

[0050] (Rate of elution from film)

From the film prepared above, a fragment of 40 mm × 40 mm was cut out, and the mass of the fragment was measured, which was the pre-immersion film mass of the film. Subsequently, the film was immersed in a 10% aqueous sulfuric acid solution at 40°C for 7 days, and was then taken out, followed by washing with water. After being dried at 50°C for 24 hours, the

mass of the film was measured again, which was the after-immersion dry film mass of the film. These mass values were substituted into the following formula to calculate the rate of elution from the film. The rate of elution from the film is preferably not higher than 5% from the viewpoint of acid resistance.

Rate of elution from film = ((pre-immersion film mass) - (after-immersion dry film mass))/(pre-immersion film mass) × 100

[0051] (Film strength retention and film stretching retention)

The film prepared above (25 mm × 100 mm) was cut out into a #2 dumbbell shape, which was then subjected to a tensile test at a temperature of 23°C and a strain rate of 200 mm/minute. Based on the maximum strength and the stretched state of a 20-mm reference line, the pre-immersion strength and the pre-immersion stretching of the film were determined. A film separately prepared (25 mm × 100 mm) was immersed in a 10% aqueous sulfuric acid solution at 40°C for 7 days, was dried at 40°C for 12 hours, and, after these immersion and drying, was cut out into a #2 dumbbell shape, which was then subjected to measurement of the strength and the stretching by the same method as above. The film strength retention and the film stretching retention were determined by the following formulae. The film strength retention and the film stretching retention are preferably from 80% to 120% from the viewpoint of acid resistance.

Film strength retention = (after-immersion dry film strength)/(pre-immersion film strength) × 100

Film stretching retention = (after-immersion dry film stretching)/(pre-immersion film stretching) × 100

The results of the evaluation are shown in Table 2.

[0052]

	Examples				Comparative Examples				
	1	2	3	4	1	2	3	4	5
Elution ratio from film (%)	0.7	0.5	0.3	0.6	1.0	0.5	0.6	1.1	1.2
Swelling ratio of film (%)	6.0	5.2	2.8	3.3	10.0	4.0	5.6	5.0	4.8
Film strength retention (%)	109	100	110	120	110	110	115	110	110
Film stretching retention (%)	100	90	90	90	80	80	80	90	95

[0053] As shown in Table 2, the film that was formed of each aqueous resin composition for forming thick film prepared in Examples 1 to 4 and received vacuum degassing treatment so that the ratio of the observed specific gravity to the theoretical specific gravity was controlled to not lower than 97% were excellent in the swelling ratio of the film, the elution ratio from the film, the film strength retention, and the film stretching retention. The same goes for the film that was formed of each aqueous resin composition for forming thick film prepared in Comparative Examples 1 to 5.

[0054] (Tests for determining conformity with quality standards C and D defined in "Technical Manual on Corrosion Prevention and Corrosion Protection for Concrete Sewage Structures" (April 2012))

<1> Appearance

A test piece was prepared in accordance with JIS K 5600-1-1:1999 (4.4), and the appearance of the test piece was visually evaluated. Preparation of the test piece was carried out by applying an aqueous resin composition for forming thick film to a flexible plate (200 mm × 150 mm × 6 mm) that was prepared in conformance with JIS A 5430:2004, and then leaving the resultant indoors for 24 hours for setting. The film thickness was designed to be 0.6 mm for the standard C, while for the standard D, the film thickness was designed to be 0.8 mm (the same film thicknesses were applied to each of the tests below).

A film free of wrinkles, irregularities, peeling-off, or breaks was evaluated as ○, and a film having wrinkles, irregularities, peeling-off, and/or breaks was evaluated as ×.

[0055] <2> Adhesion to concrete

Adhesion in a normal state and in a water-absorbed state was evaluated in accordance with JIS A 6909:2003 (7.9.2).

Evaluation of adhesion in a normal state was carried out on a test piece. The test piece was prepared by applying an aqueous resin composition for forming thick film to a cement mortar plate (70 mm × 70 mm × 20 mm) that

was prepared in conformance with JIS R 5201:1997 (10.4), and then leaving the resultant indoors for 24 hours for setting.

Evaluation of adhesion in a water-absorbed state was carried out on a test piece, which was prepared as follows. A cement mortar plate (70 mm × 70 mm × 20 mm) that was prepared in conformance with JIS R 5201:1997 (10.4) was immersed in fresh water at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 24 hours. Subsequently, a surface of the cement mortar plate was wiped with a clean cloth and, to the surface, an aqueous resin composition for forming thick film was applied. The resultant was left indoors for 24 hours for setting.

Adhesion in a normal state should not be lower than 1.5 N/mm^2 to meet either of the standards C and D. Adhesion in a water-absorbed state should not be lower than 1.2 N/mm^2 to meet either of the standards C and D.

[0056] <3> Acid resistance

Acid resistance was evaluated in accordance with JIS K 5600-6-1:1999 (7).

Evaluation of acid resistance according to the standard C was carried as follows. An aqueous resin composition for forming thick film was applied to a cement mortar plate (150 mm × 70 mm × 20 mm) that was prepared in conformance with JIS R 5201:1997 (10.4), and the resultant was left indoors for 7 days for setting, thereby giving a test piece. The test piece was immersed in a 10% aqueous sulfuric acid solution at 20°C for 45 days, and was visually observed for any swelling, break, softening, or elution in or from the film of the test piece.

Evaluation of acid resistance according to the standard D was carried as follows. An aqueous resin composition for forming thick film was applied to a cement mortar plate (150 mm × 70 mm × 20 mm) that was prepared in conformance with JIS R 5201:1997 (10.4), and the resultant was left indoors for 7 days for setting, thereby giving a test piece. The test piece was immersed in a 10% aqueous sulfuric acid solution at 20°C for 60 days, and was visually

observed for any swelling, break, softening, or elution in or from the film of the test piece.

A film free of swelling, breaks, softening, or elution was evaluated as ○, and a film having swelling, breaks, softening, and/or elution was evaluated as ×.

[0057] <4> Depth of sulfur penetration

To a cement mortar plate (150 mm × 70 mm × 20 mm) that was prepared in conformance with JIS R 5201:1997 (10.4), an aqueous resin composition for forming thick film was applied, and the resultant was left indoors for 7 days for setting, thereby giving a test piece. The test piece was immersed in a 10% aqueous sulfuric acid solution at 20°C for 120 days, and was then taken out. From the center part of the test piece, a sample having a thickness of 1 cm was cut out with a mortar-cutting cutter. Then, a polisher for use in electronic analysis was used to polish the cut surface into a mirror finish, which was then subjected to metal evaporation. The resultant was subjected to analysis, in which an electron probe microanalyzer (EPMA) was used, sulfur was used as a target element, and an image obtained by mapping was analyzed for the depth of sulfur penetration from the surface. Measurement of the depth of sulfur penetration was carried out by regarding an area with not lower than 15 counts of sulfur detected by X-ray against the background as a region where sulfur had penetrated. The measurement conditions for EPMA were as follows.

Accelerating voltage: 15 kV

Incident beam current: 100 nA ± 10 nA

Diameter of electron beam: 2 μm

Sampling duration: 50 ms

Data points: 512 points along the X axis × 512 points along the Y axis

To meet the standard C, the depth of sulfur penetration from the surface should not be greater than 10% the designed film thickness and should not be greater than 200 μm. To meet the standard D, the depth of sulfur penetration

from the surface should not be greater than 5% the designed film thickness and should not be greater than 100 μm .

[0058] <5> Alkaline resistance

Alkaline resistance was evaluated in accordance with JIS K 5600-6-1:1999 (7).

Evaluation of alkaline resistance according to the standard C was carried out as follows. An aqueous resin composition for forming thick film was applied to a cement mortar plate (150 mm $\times$ 70 mm $\times$ 20 mm) that was prepared in conformance with JIS R 5201:1997 (10.4), and the resultant was left indoors for 7 days for setting, thereby giving a test piece. The test piece was immersed in a saturated calcium hydroxide solution at 20°C for 45 days, and was visually observed for any swelling, breaking, softening, or elution in or from the film of the test piece.

Evaluation of alkaline resistance according to the standard D was carried as follows. An aqueous resin composition for forming thick film was applied to a cement mortar plate (150 mm $\times$ 70 mm $\times$ 20 mm) that was prepared in conformance with JIS R 5201:1997 (10.4), and the resultant was left indoors for 7 days for setting, thereby giving a test piece. The test piece was immersed in a saturated calcium hydroxide solution at 20°C for 60 days, and was visually observed for any swelling, break, softening, or elution in or from the film of the test piece.

A film free of swelling, breaks, softening, or elution was evaluated as ○, and a film having swelling, breaks, softening, and/or elution was evaluated as ×.

[0059] <6> Water permeability

Water permeability was evaluated in accordance with JIS A 1404:1999 (11.5).

An aqueous resin composition for forming thick film was applied to a flexible plate that was prepared in conformance with JIS A 5430:2004, and the resultant was left indoors for 24 hours for setting, thereby giving a test piece.

A pressure of 3 kgf/cm² was applied to the test piece with water, and the amount of water permeated was measured.

To meet the standard C, the amount of permeated water should not be higher than 0.20 g. To meet the standard D, the amount of permeated water should not be higher than 0.15 g.

The results of the evaluation are shown in Table 3 and Table 4. Table 3 shows the results of evaluation according to the standard C, and Table 4 shows the results of evaluation according to the standard D. For the comparative examples, only the evaluation according to the standard D was conducted.

[0060]

		Examples			
		1	2	3	4
<1> Appearance		○	○	○	○
<2> adhesion to concrete (N/mm ²)	Normal state	3.1	2.1	2.6	2.1
	Water-absorbed state	3.1	2.4	3.1	2.9
<3> Acid resistance		○	○	○	○
<4> Depth of sulfur penetration (mm)		20μm	24μm	20μm	20μm
Ratio to designed film thickness (%)		3%	4%	3%	3%
<5> Alkaline resistance		○	○	○	○
<6> Water permeability (g)		0.02	0.00	0.01	0.01

[0061]

		Examples				Comparative Examples				
		1	2	3	4	1	2	3	4	5
<1> Appearance		○	○	○	○	○	○	○	○	○
<2> Adhesion to concrete (N/mm ²)	Normal state	3.0	2.5	2.3	2.1	2.8	2.4	2.4	2.2	2.3
	Water-absorbed state	3.2	2.6	2.8	2.2	2.7	2.5	2.3	2.3	2.2
<3> Acid resistance		○	○	○	○	○	○	○	○	○
<4> Depth of sulfur penetration (mm)		30μm	24μm	30μm	30μm	150μm	120μm	110μm	85μm	80μm
Ratio to designed film thickness (%)		4%	3%	4%	4%	19%	15%	14%	11%	10%
<5> Alkaline resistance		○	○	○	○	○	○	○	○	○
<6> Water permeability (g)		0.00	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.02

[0062] As proven from Table 3 and Table 4, the films that were formed of each aqueous resin composition for forming thick film prepared in Examples 1 to 4 and received vacuum degassing treatment so that the ratio of the observed specific gravity to the theoretical specific gravity was controlled to not lower than 97% met the quality standards C and D defined in "Technical Manual on Corrosion Prevention and Corrosion Protection for Concrete Sewage Structures" (April 2012). On the other hand, the films that were formed of each aqueous resin composition for forming thick film prepared in Comparative Examples 1 to 5 failed to give acceptable results in the test for measuring the depth of sulfur penetration, indicating that the films failed to meet at least the quality standard D. Note: when the amount of a defoaming agent was increased, the ratio of the observed specific gravity to the theoretical specific gravity was successfully increased (Comparative Examples 4 and 5), but the results from the test for measuring the depth of sulfur penetration were still unacceptable.

[0063] The results above show that the present invention can provide an aqueous resin composition for forming thick film, in which the aqueous resin composition for forming thick film can form a thick film and can dry within 12 hours after application, produces no odor during application, can give a film excellent in water resistance, acid resistance, and alkaline resistance, and, in particular, can give a film that meets the quality standards C and D defined in "Technical Manual on Corrosion Prevention and Corrosion Protection for Concrete Sewage Structures" (April 2012), and that the present invention can also provide a method of producing the aqueous resin composition for forming thick film, a method of surface treatment, and a concrete structure.

[0064] This international application is based on and claims convention priority to Japanese patent application No. 2014-028218, filed February 18, 2014, the entire disclosure of which is herein incorporated by reference as a part of this international application.

CLAIMS

1. An aqueous resin composition for forming thick film, comprising a synthetic aqueous resin emulsion (A) and a filler (B), having a non-volatile content of 65% to 80% by mass, and having a ratio of observed specific gravity to theoretical specific gravity of 97% or more.
2. The aqueous resin composition for forming thick film according to claim 1, having received vacuum degassing treatment.
3. The aqueous resin composition for forming thick film according to claim 1 or 2, wherein the synthetic aqueous resin emulsion (A) is a styrene-acrylate resin emulsion.
4. The aqueous resin composition for forming thick film according to any one of claims 1 to 3, wherein the filler (B) is at least one kind selected from the group consisting of polystyrene, polyethylene, polypropylene, glass frit, glass flake, talc, and clay.
5. A method of producing an aqueous resin composition for forming thick film, the aqueous resin composition for forming thick film comprising a synthetic aqueous resin emulsion (A) and a filler (B), having a non-volatile content of 65% to 80% by mass, and having a ratio of observed specific gravity to theoretical specific gravity of 97% or more,
the method comprising:
mixing the synthetic aqueous resin emulsion (A) and the filler (B), and
then carrying out vacuum degassing treatment.
6. A method of surface treatment, comprising:

applying the aqueous resin composition for forming thick film according to any one of claims 1 to 4 to a surface of a subject to be surface-treated and then performing drying to form a film.

7. The method of surface treatment according to claim 6, wherein the subject to be surface-treated is a concrete structure.

8. A concrete structure having a protective film on a surface thereof, wherein

the protective film is obtained by applying the aqueous resin composition for forming thick film according to any one of claims 1 to 4 to a surface of a subject to be surface-treated and then performing drying.