

DESCRIPTION

TITLE

VINYL ESTER RESIN COMPOSITION, COMPOSITE MATERIAL CONTAINING SAID COMPOSITION, AND CURED PRODUCT OF SAID COMPOSITION OR COMPOSITE MATERIAL

FIELD

[0001]

The present disclosure relate to a vinyl ester resin composition, a composite material containing the composition, and a cured product of the composition or composite material.

BACKGROUND

[0002]

A vinyl ester resin is generally synthesized by using an esterification catalyst represented by a tertiary amine, a secondary amine or a salt thereof, or a quaternary ammonium salt, and, if necessary, using a radical polymerization inhibitor, an antioxidant, an ethylenically unsaturated monomer, etc., and heating and stirring a mixture of an epoxy compound having at least one epoxy group in a molecule and an unsaturated monobasic acid, such as (meth)acrylic acid, at 120 to 150°C under an oxygen atmosphere, so as not to form a gel.

[0003]

Since such a conventional vinyl ester resin often exhibits coloring, particularly yellowing, during long-term storage of the resin, particularly when a radical polymerization inhibitor or an antioxidant is used, use in applications requiring design, such as a bathtub, a kitchen counter, and a gel coat, is remarkably restricted at present. For the purpose of preventing coloration by use of such a radical polymerization inhibitor or an antioxidant, for example, Patent Literature 1 discloses a technique of adding an arylphosphine compound or a silazane compound.

[CITATION LIST]

[PATENT LITERATURE]

[0004]

[PTL1] JP 2009-249308 A

SUMMARY

[TECHNICAL PROBLEM]

[0005]

Even when the technique described in Patent Literature 1 is used, since the hue of the resin with time exhibits 1 to 4 in the number of Gardner color scale and 500 or greater in the number of

Hazen color scale, the use of a vinyl ester resin for applications accompanied by aesthetics is still limited.

[0006]

The present invention has been made based on such circumstances, and an object of the present invention is to provide a vinyl ester resin composition capable of reducing or preventing coloring over time.

[SOLUTION TO PROBLEM]

[0007]

As a result of extensive studies to solve the above problems, the present inventors have found that, by mixing a vinyl ester resin and a 1,4-benzenediol analog with a specific oxoacid, coloring of a resin over time, particularly yellowing, can be reduced or prevented more than before.

[0008]

That is, the present disclosure include the following aspects.

<Aspect 1>

A vinyl ester resin composition comprising a vinyl ester resin (A), a 1,4-benzenediol analog (B), and an oxoacid (C), wherein the oxoacid (C) is free of an ethylenically unsaturated compound and 2-oxocarboxylic acid.

<Aspect 2>

The vinyl ester resin composition according to aspect 1, further comprising an ethylenically unsaturated monomer (F).

<Aspect 3>

The vinyl ester resin composition according to aspect 1 or 2, wherein the content of the oxoacid (C) is 0.001 to 10 parts by mass with respect to 100 parts by mass of the ethylenically unsaturated component.

<Aspect 4>

The vinyl ester resin composition according to any one of aspects 1 to 3, wherein the content of the 1,4-benzenediol analog (B) is 0.001 to 0.5 parts by mass with respect to 100 parts by mass of the ethylenically unsaturated component.

<Aspect 5>

The vinyl ester resin composition according to any one of aspects 1 to 4, wherein the vinyl ester resin (A) is at least one selected from a bisphenol type vinyl ester resin, a hydrogenated bisphenol type vinyl ester resin, and a novolak phenol type vinyl ester resin.

<Aspect 6>

The vinyl ester resin composition according to any one of aspects 1 to 5, wherein the 1,4-benzenediol analog (B) is at least one selected from hydroquinone, methylhydroquinone, dimethylhydroquinone, trimethylhydroquinone, and tert-butylhydroquinone.

<Aspect 7>

The vinyl ester resin composition according to any one of aspects 1 to 6, wherein the oxoacid (C) is at least one selected from phosphorous acid, an aliphatic carboxylic acid, an aromatic carboxylic acid, a compound having a phenolic hydroxy group, and a phosphonic acid derivative.

<Aspect 8>

The vinyl ester resin composition according to any one of aspects 1 to 7, further comprising a curing accelerator (D).

<Aspect 9>

The vinyl ester resin composition according to any one of aspects 1 to 8, further comprising a radical polymerization initiator (E).

<Aspect 10>

A composite material comprising the vinyl ester resin composition according to any one of aspects 1 to 9, and at least one selected from a fiber reinforcement, a filler and an aggregate.

<Aspect 11>

A cured product of the vinyl ester resin composition according to any one of aspects 1 to 9 or the composite material according to aspect 10.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0009]

According to the present disclosure, it is possible to provide a vinyl ester resin composition capable of reducing or preventing coloring over time as compared with a conventional vinyl ester resin composition.

DESCRIPTION OF EMBODIMENTS

[0010]

Hereinafter, the contents of the present disclosure will be described in further detail.

[0011]

<<Vinyl ester resin composition>>

The vinyl ester resin composition contains a vinyl ester resin (A), a 1,4-benzenediol analog (B), and an oxoacid (C), and the oxoacid (C) is free of an ethylenically unsaturated compound and a 2-oxocarboxylic acid.

[0012]

<Vinyl ester resin (A)>

In general, the vinyl ester resin (A) is a compound having a polymerizable unsaturated bond obtained by ring-opening reaction of an epoxy group in an epoxy compound (a) having 2 or more epoxy groups with a carboxy group of an unsaturated monobasic acid (b) having a polymerizable unsaturated bond and a carboxy group. Such a vinyl ester resin (A) is described, for example, in

“Polyester Resin Handbook” (The Nikkan Kogyo Shimbun, Ltd., published in 1988). In the context of the present disclosure, the vinyl ester resin (A) and the ethylenically unsaturated monomer (F) as an optional component described later may be collectively referred to as “ethylenically unsaturated component”. In other words, when the ethylenically unsaturated monomer (F), which is an optional component, is not contained in the vinyl ester resin composition, only the vinyl ester resin (A) is intended to be an ethylenically unsaturated component, and when the ethylenically unsaturated monomer (F) is contained, a combination of the vinyl ester resin (A) and the ethylenically unsaturated monomer (F) is intended to be an ethylenically unsaturated component.

[0013]

(Epoxy compound (a))

The epoxy compound (a) is not particularly limited as long as it is a compound having two or more epoxy groups. For example, at least one selected from a bisphenol type epoxy compound, a hydrogenated bisphenol type epoxy compound, and a novolak phenol type epoxy compound can be used. Such an epoxy compound can further improve the mechanical strength and corrosion resistance of a cured product.

[0014]

Examples of the bisphenol type epoxy compound include those obtained by reacting a bisphenol compound, such as bisphenol A, bisphenol F, bisphenol S and tetrabromobisphenol A, with epichlorohydrin or methylepichlorohydrin, or those obtained by reacting a glycidyl ether of bisphenol A and a condensation product of the above bisphenol compound with epichlorohydrin or methylepichlorohydrin.

[0015]

Examples of the hydrogenated bisphenol type epoxy compound include those obtained by reacting a glycidyl ether of hydrogenated bisphenol A with a bisphenol compound, such as bisphenol A, bisphenol F, bisphenol S, and tetrabromobisphenol A.

[0016]

Examples of the novolak phenol type epoxy compound include those obtained by reacting phenol novolak or cresol novolak with epichlorohydrin or methylepichlorohydrin.

[0017]

(Unsaturated monobasic acid (b))

The unsaturated monobasic acid (b) is not particularly limited as long as it is a monocarboxylic acid having a polymerizable unsaturated bond. For example, the unsaturated monobasic acid (b) is preferably at least one selected from acrylic acid, methacrylic acid, crotonic acid, and cinnamic acid, more preferably acrylic acid or methacrylic acid, and particularly preferably methacrylic acid. Since the vinyl ester resin (A) obtained by the reaction of methacrylic acid and the epoxy compound (a) has high hydrolysis resistance against acid and alkali, the corrosion resistance of a cured product thereof can be further improved.

[0018]

The amount of the unsaturated monobasic acid (b) used in the ring-opening reaction of the epoxy compound (a) and the unsaturated monobasic acid (b) is preferably 0.3 to 1.5 equivalents, more preferably 0.4 to 1.2 equivalents, and particularly preferably 0.5 to 1.0 equivalents, with respect to one equivalent of the epoxy group of the epoxy compound (a). When the amount of the unsaturated monobasic acid (b) used is in the range of 0.3 to 1.5 equivalents with respect to one equivalent of the epoxy group of the epoxy compound (a), a cured product having a sufficient hardness can be obtained by the radical polymerization reaction of the vinyl ester resin composition.

[0019]

(Synthesis method of vinyl ester resin (A))

The vinyl ester resin (A) can be synthesized by a known synthetic method. Examples thereof include a method in which the epoxy compound (a) and the unsaturated monobasic acid (b) are dissolved in a solvent (G) as needed, and the mixture is reacted at 70 to 150°C, preferably 80 to 140°C, and more preferably 90 to 130°C, in the presence of an esterification catalyst and optionally a 1,4-benzenediol analog (B) described below.

[0020]

The unreacted unsaturated monobasic acid (b) after synthesizing the vinyl ester resin (A) is regarded as an ethylenically unsaturated monomer (F) described later. Unsaturated monobasic acids, such as acrylic acid, methacrylic acid, and cinnamic acid, are also oxoacids, but such unreacted unsaturated monobasic acids (b) are not included in the oxoacid (C) and are regarded as ethylenically unsaturated monomers (F).

[0021]

There is no particular limitation on the esterification catalyst. For example, one or more known catalysts, such as tertiary amines, including triethylamine, N,N-dimethylbenzylamine, N,N-dimethylaniline and diazabicyclooctane; phosphorus compounds, including triphenylphosphine, benzyltriphenylphosphonium chloride; or diethylamine hydrochloride, can be used.

[0022]

<1,4-benzenediol analogue (B)>

The 1,4-benzenediol analog (B) is a compound having a 1,4-benzenediol structure and is commonly used as a radical polymerization inhibitor. One or more kinds of the analogs (B) may be used, and are not particularly limited. Examples thereof include hydroquinone (1,4-benzenediol), and those with one or more alkyl groups having 1 to 12 carbon atoms on the benzene ring of 1,4-benzenediol. Among these, at least one selected from hydroquinone, methylhydroquinone, dimethylhydroquinone, trimethylhydroquinone, and tert-butylhydroquinone is preferable.

[0023]

As the 1,4-benzenediol analog (B), a commercially available one may be used as appropriate,

and may be dissolved in a solvent (G) described later and used. Such a 1,4-benzenediol analog (B) may be simultaneously blended at the time of synthesis of the vinyl ester resin (A), may be mixed with the vinyl ester resin (A) after synthesis and the oxoacid (C), or may be used in both cases. It is preferable to simultaneously blend the 1,4-benzenediol analog (B) at the time of synthesis of the vinyl ester resin (A). In one embodiment, at least a portion of the 1,4-benzenediol analog (B) used in the synthesis of the vinyl ester resin (A) is contained in the vinyl ester resin composition containing the vinyl ester resin (A) and the oxoacid (C).

[0024]

The content of the 1,4-benzenediol analog (B) is not particularly limited. For example, the content of the 1,4-benzenediol analog (B) is preferably 0.001 to 0.5 parts by mass, more preferably 0.005 to 0.1 parts by mass, and particularly preferably 0.01 to 0.05 parts by mass, with respect to 100 parts by mass of the ethylenically unsaturated component. When the content of the 1,4-benzenediol analog (B) is within such a range, it is possible to obtain an effect of reducing or preventing yellowing over time without extremely delaying curing of the resin composition while maintaining a realistic pot life.

[0025]

<Oxoacid (C)>

The vinyl ester resin composition contains an oxoacid (C). However, the oxoacid (C) does not include an ethylenically unsaturated compound and a 2-oxocarboxylic acid. An ethylenically unsaturated compound which also falls under the ethylenically unsaturated monomer (F) is defined as the ethylenically unsaturated monomer (F). The oxoacid (C) contributes to the reduction or prevention of coloration of the resin over time, particularly yellowing, due to the 1,4-benzenediol analog (B) acting as a radical polymerization inhibitor.

[0026]

One or more kinds of the oxoacids (C) may be used, and are not limited to the following. For example, the oxoacid (C) is preferably phosphorous acid or an organic oxoacid. Among them, the oxoacid (C) is more preferably at least one selected from phosphorous acid, a saturated aliphatic carboxylic acid, an aromatic carboxylic acid, a compound having a phenolic hydroxy group, and a phosphonic acid derivative.

[0027]

Specific examples of the organic oxoacid include saturated aliphatic carboxylic acids, such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, heptanoic acid, octanoic acid (octylic acid), nonanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, margaric acid, and stearic acid; hydroxy acids, such as lactic acid, malic acid, and citric acid; aromatic carboxylic acids, such as benzoic acid, orthophthalic acid, isophthalic acid, terephthalic acid, salicylic acid, gallic acid, and mellitic acid; saturated dicarboxylic acids, such as oxalic acid, malonic acid, succinic acid, glutaric acid, and adipic acid; tricarboxylic acids, such as aconitic acid;

aliphatic carboxylic acids, such as amino acids other than 2-oxoaminocarboxylic acid; phenols and derivatives thereof, compounds having a phenolic hydroxy group, such as catechols, including catechol, methylcatechol, ethylcatechol, propylcatechol, and butylcatechol, and derivatives thereof; and phosphonic acid derivatives, such as methylphosphonic acid, ethylphosphonic acid, propylphosphonic acid, butylphosphonic acid and phenylphosphonic acid.

[0028]

Since a 2-oxocarboxylic acid, which is a kind of oxoacids, has low stability under a temperature higher than or equal to room temperature and causes coloring due to decomposition, etc., during polymerization, it is desirable not to add it in order to reduce or prevent coloring. However, it may be contained in the composition as long as it does not affect coloring over time. Specifically, the content of the 2-oxocarboxylic acid in the vinyl ester resin composition is preferably 0.1% by mass or less, more preferably 0.05% by mass or less, and particularly preferably 0.01% by mass or less.

[0029]

Specific examples of the 2-oxocarboxylic acid include pyruvic acid, 3-bromopyruvic acid, 2-oxobutyric acid, oxamic acid, 2-oxoglutaric acid, glyoxylic acid, N,N-dimethyloxamic acid, and oxaloacetic acid.

[0030]

A commercially available oxoacid (C) may be used as appropriate, and may be dissolved in a solvent (G) described later and used. Such an oxoacid (C) may be simultaneously blended at the time of synthesizing the vinyl ester resin (A), may be mixed together with the obtained vinyl ester resin (A), or may be used in both cases. From the viewpoint of an effect reducing or preventing yellowing, it is preferable to mix together with the obtained vinyl ester resin (A). In one embodiment, at least a portion of the oxoacid (C) used in the synthesis of the vinyl ester resin (A) is contained in the vinyl ester resin composition.

[0031]

The content of the oxoacid (C) is not particularly limited. For example, the content of the oxoacid (C) is preferably 0.001 to 10 parts by mass, more preferably 0.005 to 5 parts by mass, and particularly preferably 0.01 to 1 parts by mass, with respect to 100 parts by mass of the ethylenically unsaturated component. When the content of the oxoacid (C) is within such a range, it is possible to obtain an effect of reducing or preventing yellowing over time without extremely delaying curing of the resin composition while maintaining a realistic pot life.

[0032]

<Curing accelerator (D)>

The vinyl ester resin composition may include one or more curing accelerators (D) to accelerate the radical polymerization reaction of the composition. There is no particular limitation on the curing accelerator (D). For example, a salt of a metal element and an organic acid is

preferable. Examples of the metal element include cobalt, vanadium, and manganese. Specific examples of such a curing accelerator (D) include cobalt naphthenate, cobalt octylate, zinc octylate, vanadium octylate, copper naphthenate, and barium naphthenate.

[0033]

Examples of the curing accelerator (D) other than the above include metal chelating compounds, such as vanadium acetylacetonate, cobalt acetylacetonate, and iron acetylacetonate; aniline; N,N-substituted anilines, such as N,N-dimethylaniline; p-toluidine; N,N-substituted-p-toluidine, such as N,N-dimethyl-p-toluidine, and N,N-bis(2-hydroxyethyl)-p-toluidine; 4-(N,N-substituted amino)benzaldehydes, such as 4-(N,N-dimethylamino)benzaldehyde, and 4-[N,N-bis(2-hydroxyethyl)amino]benzaldehyde; amine compounds, such as triethanolamine, diethylenetriamine, pyridine, phenylmorpholine, and piperidine; and β -diketones, such as acetylacetone, methyl acetoacetate, ethyl acetoacetate, acetylbutyllactone, and dimethylacetoacetamide. These curing accelerators (D) may be used in combination with the above-mentioned salts of metal elements and organic acids.

[0034]

The amount of the curing accelerator (D) added is preferably 0.01 to 6.0 parts by mass, more preferably 0.05 to 4.0 parts by mass, and particularly preferably 0.1 to 3.0 parts by mass, with respect to 100 parts by mass of the ethylenically unsaturated component. When the amount of the curing accelerator (D) added is in such a range, the radical polymerization reaction of the vinyl ester resin composition can be rapidly proceeded even at a low temperature to an ordinary temperature, for example, in a temperature range of 5 to 40°C.

[0035]

<Radical polymerization initiator (E)>

The vinyl ester resin composition may include one or more radical polymerization initiators (E) as a curing agent in order to cure the composition. When the radical polymerization initiator (E) is added to the vinyl ester resin composition, curing of the composition starts. Therefore, for example, when the vinyl ester resin composition is stored, it is desirable that the radical polymerization initiator (E) be added to the composition immediately before curing the vinyl ester resin composition.

[0036]

The radical polymerization initiator (E) may be appropriately selected depending on the application, the curing condition, etc., and is not particularly limited. For example, a known thermal radical initiator or a photoradical initiator can be used, and among them, a thermal radical initiator is preferable.

[0037]

Examples of the thermal radical initiator include diacyl peroxides, such as benzoyl peroxide; peroxy esters, such as t-butyl peroxybenzoate; hydroperoxides, such as cumene hydroperoxide;

dialkyl peroxides, such as dicumyl peroxide; ketone peroxides, such as methyl ethyl ketone peroxide, acetylacetone peroxide; and organic peroxides, such as peroxyketals, alkyl peresters, and percarbonates.

[0038]

The amount of the radical polymerization initiator (E) added is preferably from 0.1 to 10.0 parts by mass, more preferably from 0.2 to 6.0 parts by mass, and particularly preferably from 0.3 to 3.5 parts by mass, with respect to 100 parts by mass of the ethylenically unsaturated component. Within such a range, since the radical polymerization reaction of the vinyl ester resin composition proceeds, a cured product having sufficient hardness can be obtained.

[0039]

<Ethylenically unsaturated monomer (F)>

The vinyl ester resin composition may include an ethylenically unsaturated monomer (F) as an optional component. The ethylenically unsaturated monomer (F) is not particularly limited as long as it is a compound having an ethylenically unsaturated group. For example, vinyl compounds, such as styrene, vinyltoluene, t-butylstyrene, methoxystyrene, divinylbenzene, vinyl naphthalene, and acenaphthylene; (meth)acrylates, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, tridecyl (meth)acrylate, stearyl (meth)acrylate, cyclohexyl (meth)acrylate, furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, allyl (meth)acrylate, isobornyl (meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, tricyclodecanol di(meth)acrylate, and trimethylolpropane tri(meth)acrylate; unsaturated fatty acids, such as oleic acid, linoleic acid, linolenic acid, arachidonic acid, eicosapentaenoic acid, docosahexaenoic acid, and sorbic acid; unsaturated dicarboxylic acids, such as fumaric acid and maleic acid; cinnamic acid; dihydroxycinnamic acid, etc., or a combination thereof may be used. “(Meth)acrylate” is herein referred to as including “acrylate” and “methacrylate”.

[0040]

The content of the ethylenically unsaturated monomer (F) is preferably 13 to 60% by mass, more preferably 20 to 55% by mass, and still more preferably 23 to 50% by mass, based on the ethylenically unsaturated component. When the content of the ethylenically unsaturated monomer (F) is 13 to 60% by mass, the mechanical strength of the cured product can be improved.

[0041]

<Solvent (G)>

Examples of the solvent used for synthesizing the vinyl ester resin (A) include organic solvents, such as esters including n-butyl acetate and n-propyl acetate; and aromatic hydrocarbons

including benzene, toluene, and xylene. As the solvent, the above-mentioned ethylenically unsaturated monomer (F), such as styrene, may be used. The content of the solvent is preferably 5 to 60 parts by mass, more preferably 10 to 50 parts by mass, and still more preferably 20 to 40 parts by mass, with respect to 100 parts by mass of the ethylenically unsaturated component.

[0042]

<Additive (H)>

In the vinyl ester resin composition, one or more additives may be appropriately blended within a range that does not affect the effect of the present invention or within a range that does not reduce the mechanical strength, etc., of the cured product.

[0043]

Examples of the additive include a thixotropic imparting agent, a thixotropic imparting aid, a thickener, a colorant, a plasticizer, and a wax.

[0044]

(Thixotropic imparting agent)

Examples of the thixotropic imparting agent include inorganic powders, such as silica and clay.

[0045]

(Thixotropic imparting aid)

Examples of the thixotropic imparting aid include polyethylene glycol, glycerin, polyhydroxycarboxylic acid amides, organic quaternary ammonium salts, and BYK-R-605 (manufactured by BYK Japan KK).

[0046]

(Thickener)

Examples of the thickener include metal oxides, such as magnesium oxide, calcium oxide, and zinc oxide, and metal hydroxides, such as magnesium hydroxide and calcium hydroxide.

[0047]

(Colorant)

Examples of the colorant include an organic pigment, an inorganic pigment, and a dye.

[0048]

(Plasticizer)

Examples of the plasticizer include chlorinated paraffin, phosphoric esters, and phthalic esters.

[0049]

(Wax)

The wax can be added for the purpose of improving the surface drying property due to the air blocking effect on the surface of the cured product. Examples of the wax include petroleum wax, olefin wax, polar wax, and special wax.

[0050]

<Measurement of the number of Hazen color scale>

The coloring of the vinyl ester resin composition over time can be evaluated by an increase rate of the number of Hazen color scale. The number of Hazen color scale can be measured by a color-difference meter. The “increase rate” is a value calculated from the following formula (1):

$$\text{Increase rate (\%)} = (\text{color number after 14 days} - \text{initial color number}) \times 100 / \text{initial color number} \quad (1)$$

[0051]

For example, an increase rate of the number of Hazen color scale after 14 days in a sealed system containing air at 50°C is preferably 500% or less, more preferably 450% or less, and particularly preferably 400% or less. The lower limit value of the increase rate is not particularly limited, but may be defined as 0% or greater, 1% or greater, or 2% or greater.

[0052]

<<Composite material>>

A composite material can be obtained by combining at least one selected from, for example, a fiber reinforcing material, a filler, and an aggregate with the vinyl ester resin composition.

[0053]

<Fiber reinforcing material t>

Examples of the fiber reinforcing material include organic or inorganic and synthetic or natural fiber reinforcing materials, such as glass fibers, carbon fibers, polyester fibers, aramid fibers, vinylon fibers, and cellulose nanofibers.

[0054]

As the fiber reinforcing material, for example, a short fiber, a long fiber, a twist yarn, a chop, a chopped strand mat, a continuous strand mat, a roving, a nonwoven fabric, such as a spunbond nonwoven fabric or a meltblown nonwoven fabric, a woven fabric, such as a roving cloth, a plain weave, a satin weave or a twill weave, a braid, a three dimensional fabric, or a three dimensional braid can be used.

[0055]

The content of the fiber reinforcing material can be appropriately determined depending on the use application and the required performance of the composite material, and is not particularly limited. For example, the content of the fiber reinforcing material may be 0.1 to 500 parts by mass with respect to 100 parts by mass of the vinyl ester resin composition.

[0056]

(Filler)

Examples of the filler include calcium carbonate, aluminum hydroxide, fly ash, barium sulfate, talc, clay, glass powder, and wood powder. A hollow filler, such as a glass microballoon, a microballoon of a saran resin, a microballoon of acrylonitrile, and a silas balloon can also be used.

[0057]

The content of the filler can be appropriately determined depending on the use application and

the required performance of the composite material, and is not particularly limited. For example, the amount may be 10 to 500 parts by mass with respect to 100 parts by mass of the vinyl ester resin composition.

[0058]

(Aggregate)

Examples of the aggregate include general aggregates, such as silica sand, crushed stone, and gravel, and synthetic aggregates synthesized from incineration ash, etc., and lightweight aggregates.

[0059]

The content of the aggregate can be appropriately determined depending on the use application and the required performance of the composite material, and is not particularly limited. For example, the content of the aggregate may be 10 to 500 parts by mass with respect to 100 parts by mass of the vinyl ester resin composition.

[0060]

<<Cured product>>

A cured product is obtained by curing the vinyl ester resin composition or the composite material.

[0061]

<Method of curing vinyl ester resin composition and composite material>

The vinyl ester resin composition and the composite material can be cured by a known method.

[0062]

As a curing method of the vinyl ester resin composition or the composite material, for example, a method of adding a radical polymerization initiator (E) to the vinyl ester resin composition or the composite material and curing it under normal temperature or by heating, a method of curing the composite material prepared using the vinyl ester resin composition containing a radical polymerization initiator (E) under normal temperature or by heating, a method of adding a curing accelerator (D) to the vinyl ester resin composition or the composite material and mixing it, and then further adding thereto a radical polymerization initiator (E) and curing the mixture under normal temperature or by heating, or a method of curing the composite material prepared using the vinyl ester resin composition prepared by further adding a radical polymerization initiator (E) after adding and mixing a curing accelerator (D), at normal temperature or heating, may be used. A specific temperature range of normal temperature and heating can be, for example, a temperature range of about 15 to 200°C.

[0063]

<<Method of using vinyl ester resin composition and composite material>>

Use of the vinyl ester resin composition and the composite material is not particularly limited. For example, they can be used as a raw material for a general fiber-reinforced plastic (hereinafter, referred to as “FRP”) which is applied to a pipe of a chemical plant, a chemical liquid storage tank,

a concrete repair material, etc. They can exhibit an action capable of reducing or preventing coloring over time, and therefore, they are particularly preferably used as various materials for applications requiring design, such as a bathtub, a kitchen counter, and a gel coat.

[0064]

The method of molding FRP may be appropriately selected depending on the purpose, and is not particularly limited. Examples thereof include a method in which the vinyl ester resin composition is applied or machine-molded while being impregnated into a fiber reinforcing material, and cured, or a method in which the composite material is applied or machine-molded, and cured.

[0065]

Examples of the method in which the vinyl ester resin composition is applied or machine-molded while being impregnated into a fiber reinforcing material, and cured, include a hand lay-up molding method, a resin transfer molding method, and a vacuum assisted resin transfer molding method.

[0066]

The vinyl ester resin composition can be applied using known coating means, such as a brush, a roll, a trowel, a spatula, and a syringe.

[0067]

Examples of the method in which the composite material is applied or machine-molded, and cured, include a spray-up molding method, a filament winding molding method, a sheet winding molding method, a pull-out molding method, and an injection molding method.

EXAMPLES

[0068]

<<Examples 1 to 7 and Comparative Examples 1 to 2>>

Hereinafter, the present invention will be described based on the Examples, but the present invention is not limited by the Examples.

[0069]

<Preparation of vinyl ester resin composition>

A vinyl ester resin composition was prepared by the following procedure.

[0070]

(Example 1)

To a 1 L 4-necked flask equipped with a thermometer, a stirrer, a reflux condenser, and a gas inlet, 434.5 g of Araldite (registered trademark) AER-2603 (Asahi Kasei E-Materials Co., Ltd.) which is a bisphenol A type epoxy resin with an epoxy equivalent of 188.0, 125.3 g of styrene, and 66.3 g of acrylic acid in which 0.13 g of hydroquinone was dissolved were charged and heated while stirring. At the time of reaching 100 to 110°C, 132.7 g of acrylic acid in which 1.9 g of

benzyltriphenylphosphonium chloride (TPP-ZC, manufactured by Hokko Chemical Industry Co., Ltd.) was dissolved and added dropwise into the 4-necked flask over a period of about 30 minutes and reacted at 130°C. When the acid value reached 11 mg KOH/g or less, the mixture was cooled, and when the temperature reached 110°C or less, 438.6 g of styrene was added, thereby synthesizing a bisphenol A type vinyl ester resin (VE-1) and preparing a solution containing the resin (VE-1). In the solution, the content of styrene in the ethylenically unsaturated component was 47% by mass, and the amount of hydroquinone with respect to 100 parts by mass of the ethylenically unsaturated component was 0.011 parts by mass.

[0071]

A vinyl ester resin composition was prepared by adding and mixing phosphorous acid to a solution containing the obtained vinyl ester resin (VE-1) so that 0.1 parts by mass of phosphorous acid, which is an oxoacid, was contained with respect to 100 parts by mass of the total of the vinyl ester resin (VE-1) and styrene, which are ethylenically unsaturated components in the solution.

[0072]

(Examples 2 to 6 and Comparative Examples 1 to 2)

The vinyl ester resin compositions of Examples 2 to 6 and Comparative Examples 1 to 2 were prepared by the same method as in Example 1, respectively, except that the oxoacid described in Table 1 was used in Examples 2 to 6 and Comparative Example 2, and the oxoacid was not used in Comparative Example 1.

[0073]

The coloring properties of the vinyl ester resin compositions of Examples 1 to 6 and Comparative Examples 1 to 2 were evaluated from the number of Hazen color scale by the following measurement method.

[0074]

<Measurement of the number of Hazen color scale>

The obtained vinyl ester resin composition was injected into a colorless, transparent, round-bottom glass tube with a total length of 165 mm and an inside diameter of 13 mm to a height of 70 mm from the bottom, and the remaining space was filled with air to prepare a sample for measurement, and the number of Hazen color scale of the sample was measured by a color-difference meter (ZE, manufactured by Nippon Denshoku Industries Co., Ltd.). The results are shown in Table 1. The “initial color number” in Table 1 is the number of Hazen color scale of the vinyl ester resin composition measured within 1 hours after the preparation of the sample for measurement, and the “color number after 14 days” is the number of Hazen color scale of the vinyl ester resin composition after sealing the upper portion of the glass tube of the sample for measurement with a silicone stopper and storing at 50°C for 2 weeks, and the “increase rate” is a value calculated from the following formula (1) as described above:

Increase rate (%) = (color number after 14 days - initial color number) × 100 / initial color number

(1)

[0075]

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2
Oxoacid	Phosphorous acid	Phenylphosphonic acid	Acetic acid	octylic acid	Citric acid	Lactic acid	-	Pyruvic acid
Initial color number	26	28	25	21	23	23	27	23
Color number after 14 days	27	52	135	125	86	148	181	439
Increase rate (%)	3.8	92	420	400	240	480	590	1600

[0076]

(Example 7)

As a radical polymerization initiator, 1.0 parts by mass of benzoyl peroxide was added to 100 parts by mass of the vinyl ester resin composition obtained in Example 2, and the curability was measured by a procedure in conformity with 80°C high temperature curing characteristics (Method A) defined by 5.7.1 of JIS K 6901. The results are shown in Table 2.

[0077]

[Table 2]

	Example 7
Gelation time (min)	11.2
Minimum curing time (min)	15.0
Maximum generated heat temperature (°C)	204

[0078]

(Results)

From the results of Examples 1 to 6 and Comparative Examples 1 to 2, it is clear that yellowing of the resin due to long-term storage can be reduced or prevented by the addition of oxoacid (C). From the results of Example 7, it can be confirmed that the vinyl ester resin composition of the present invention has good curability.

[Industrial applicability].

[0079]

The vinyl ester resin composition according to the present disclosure is widely used in the fields of molding materials for FRP, molding materials for casting, lining materials, paints, adhesives, etc. The vinyl ester resin composition has an effect of reducing or preventing coloring over time, and thus can be suitably used, in particular, in the field of applications requiring design, such as bathtubs, kitchen counters, and gel coats.

CLAIMS

[Claim 1]

A vinyl ester resin composition comprising a vinyl ester resin (A), a 1,4-benzenediol analog (B), and an oxoacid (C), wherein the oxoacid (C) is free of an ethylenically unsaturated compound and 2-oxocarboxylic acid.

[Claim 2]

The vinyl ester resin composition according to claim 1, further comprising an ethylenically unsaturated monomer (F).

[Claim 3]

The vinyl ester resin composition according to claim 1 or 2, wherein the content of the oxoacid (C) is 0.001 to 10 parts by mass with respect to 100 parts by mass of the ethylenically unsaturated component.

[Claim 4]

The vinyl ester resin composition according to any one of claims 1 to 3, wherein the content of the 1,4-benzenediol analog (B) is 0.001 to 0.5 parts by mass with respect to 100 parts by mass of the ethylenically unsaturated component.

[Claim 5]

The vinyl ester resin composition according to any one of claims 1 to 4, wherein the vinyl ester resin (A) is at least one selected from a bisphenol type vinyl ester resin, a hydrogenated bisphenol type vinyl ester resin, and a novolak phenol type vinyl ester resin.

[Claim 6]

The vinyl ester resin composition according to any one of claims 1 to 5, wherein the 1,4-benzenediol analog (B) is at least one selected from hydroquinone, methylhydroquinone, dimethylhydroquinone, trimethylhydroquinone, and tertiary butylhydroquinone.

[Claim 7]

The vinyl ester resin composition according to any one of claims 1 to 6, wherein the oxoacid (C) is at least one selected from a phosphorous acid, an aliphatic carboxylic acid, an aromatic carboxylic acid, a compound having a phenolic hydroxy group, and a phosphonic acid derivative.

[Claim 8]

The vinyl ester resin composition according to any one of claims 1 to 7, further comprising a curing accelerator (D).

[Claim 9]

The vinyl ester resin composition according to any one of claims 1 to 8, further comprising a radical polymerization initiator (E).

[Claim 10]

A composite material comprising the vinyl ester resin composition according to any one of

claims 1 to 9, and at least one selected from a fiber reinforcement, a filler and an aggregate.

[Claim 11]

A cured product of the vinyl ester resin composition according to any one of claims 1 to 9 or the composite material according to claim 10.