DESCRIPTION

OXIDATIVE CURING ALKYD-MODIFIED SILICONE ACRYLIC COPOLYMER

TECHNICAL FIELD

[0001]

The present invention relates to an oxidative curing alkyd-modified silicone acrylic copolymer capable of forming a coating film that is excellent in initial gloss, weather resistance, initial drying properties, and impact resistance (strength).

BACKGROUND ART

[0002]

An alkyd resin is basically composed of oil and fat, and has oxidative polymerization properties with which the alkyd resin is naturally cured into a coating film by oxidative drying. It is therefore possible to obtain the coating film with initial gloss that is dried earlier than oil ready mixed paint using boiled oil (long oil) as a coating film forming ingredient. The alkyd resin is widely used as a coating film forming ingredient of ready mixed synthetic resin paint for use in indoor and outdoor iron parts and indoor wood parts of general buildings. However, the alkyd resin has superior initial gloss but dries slower than acrylic resins and silicone-modified resins. Hence, portions exposed to ultraviolet rays,

wind and rain cause deterioration in weather resistance and coating film strength. Thus, the range of application of paint using the alkyd resin needs to be limited to indoor parts as much as possible.

[0003]

As a method for solving the problem of weather resistance, Patent Document 1 describes a one-pack type coating composition containing a copolymer in which cyclohexyl methacrylate that is a kind of high weather resistant monomers is used for a fatty acid modified acrylic resin and a fatty acid modified acrylic copolymer portion.

[0004]

Patent Document 2 describes an oxidative curing silicone-modified (meth)acrylic copolymer obtained by adding fatty acid to an epoxy group of an epoxy group-containing acrylic copolymer, and reacting a silicone with a hydroxyl group generated by a ring opening of an epoxy group.

[0005]

Patent Document 3 describes a nonaqueous dispersion type resin whose weather resistance is improved by generating a vinyl copolymer (A) that is less apt to dissolve in an organic solvent generating by subjecting a vinyl-type monomer to copolymerization in the presence of a polymer (B) to be dissolved in the organic solvent, and subjecting the vinyl copolymer (A) to silicone

modification. Patent Document 3 further describes that the polymer (B) may be an oil modified alkyd having at least a 50% oil length.

[0006]

Patent Document 4 describes an oxidative curing silicone-modified vinyl copolymer using a polysiloxane-containing vinyl monomer, and describes that oxidative polymerization properties are ensured by introducing an unsaturated fatty acid into a copolymer molecule, and carrying out modification with an unsaturated alkyd resin.

[0007]

Patent Document 5 describes a resin that is obtained by mixing and reacting a copolymer obtained by subjecting different monomers to radical copolymerization, an alkyd resin, and polysiloxane together. Patent Document 5 describes that the resin is basically used as a lacquer, together with a crosslinking binder, such as polyisocyanate, and describes that it is also possible to impart oxidative curing properties.

RELATED ART DOCUMENT

PATENT DOCUMENTS

[0008]

Patent Document 1: Japanese Unexamined Patent Publication No. 2004-211009;

Patent Document 2: Japanese Unexamined Patent Publication No. 2001-122968;

Patent Document 3: Japanese Unexamined Patent

Publication No. 10-158311;

Patent Document 4: Japanese Unexamined Patent Publication No. 2004-091678; and

Patent Document 5: Japanese Unexamined Patent Publication No. 55-005977

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009]

The copolymer described in Patent Document 1 contains the fatty acid that is a low polarity soft ingredient as a constituent monomer. Therefore, a coating composition containing the copolymer is insufficient for imparting weather resistance to a coating film.

[0010]

The oxidative curing silicone-modified (meth)acrylic copolymer described in Patent Document 2 has satisfactory weather resistance. However, the initial gloss of the coating film is insufficient, and solubility into a solvent is lowered due to the modification with the silicone.

[0011]

In the nonaqueous dispersion type resin described in Patent Document 3, the polymer (B) used as a dispersion stabilizer merely surrounds the polymer (A) that constitutes the interior of the resin. That is, the polymers (A) and (B) are not bonded together. Therefore,

a problem remains in terms of the weather resistance of the coating film. There is also a fateful problem of the nonaqueous dispersion that the initial gloss of the coating film is insufficient.

[0012]

The oxidative curing silicone-modified vinyl copolymer described in Patent Document 4 is insufficient for imparting weather resistance and initial gloss to the coating film.

[0013]

In the process for producing the resin described in Patent Document 5, the previously polymerized vinyl copolymer is reacted with the alkyd resin and polysiloxane. Accordingly, the alkyd resin and the copolymer are not structurally directly bonded together but are bonded together via the polysiloxane. This leads to poor balance among the alkyd resin, the copolymer, and the polysiloxane. The crosslinking reaction is less likely to proceed during the coating film formation, resulting in insufficient weather resistance and impact resistance (strength) of the coating film.

[0014]

An object of the present invention is to provide an oxidative curing alkyd-modified silicone acrylic copolymer serving as a coating film forming ingredient. The oxidative curing alkyd-modified silicone acrylic copolymer ensures high initial gloss of a coating film,

which has not been achieved by the resins and copolymers respectively disclosed in Patent Documents 1 to 5, or by conventional silicone-modified resins, and also satisfies weather resistance, initial drying properties, and impact resistance (strength) in terms of which the alkyd resin is inferior to the conventional silicone-modified resin.

MEANS FOR SOLVING THE PROBLEMS

[0015]

As a result of intensive studies to solve the above problems, the present inventor has completed the present invention by finding out solutions made of the following structures.

(1) An oxidative curing alkyd-modified silicone acrylic copolymer obtained by reacting an oxidative curing acrylic copolymer (a) obtained by graft polymerizing monomers illustrated in the following (a-1), (a-2), and (a-3) into an alkyd resin (c) having an oxidative polymerizable group, and a silicone (b) having at least one of a hydroxyl group and an alkoxy group. In a raw material, 8 to 40% by mass of the alkyd resin (c), 10 to 30% by mass of the styrenes (a-1), and 5 to 15% by mass of the silicone (b) are contained in a total amount of the alkyd resin (c), the styrenes (a-1), the (meth)acrylic acid ester (a-2), the polymerizable unsaturated monomer (a-3), and the silicone (b).

(a-1) styrenes;

(a-2) a (meth)acrylic acid ester; and

(a-3) a polymerizable unsaturated monomer having at least one of functional group selected from the group consisting of a hydroxyl group, a carboxyl group, a glycidyl group, and an isocyanate group.

(2) The oxidative curing alkyd-modified silicone acrylic copolymer as described in the above (1), wherein the styrenes (a-1), the (meth)acrylic acid ester (a-2), and the polymerizable unsaturated monomer (a-3) are respectively contained in following proportions in a total amount of the styrenes (a-1), the (meth)acrylic acid ester (a-2), and the polymerizable unsaturated monomer (a-3).

(a-1) the styrenes: 13 to 40% by mass;

(a-2) the (meth)acrylic acid ester: 53 to 86% by mass; and

(a-3) the polymerizable unsaturated monomer: 1 to 7% by mass

(3) The oxidative curing alkyd-modified silicone acrylic copolymer as described in the above (1) or (2), wherein the styrenes (a-1), the (meth)acrylic acid ester (a-2), and the polymerizable unsaturated monomer (a-3) are contained in a proportion of 45 to 87% by mass in total in the oxidative curing alkyd-modified silicone acrylic copolymer.

(4) The oxidative curing alkyd-modified silicone acrylic copolymer as described in any one of the above (1) to (3), having a solid iodine value of 5 to 50.

(5) The oxidative curing alkyd-modified silicone acrylic copolymer as described in any one of the above (1) to (4), having a weight average molecular weight of 10,000 to 150,000.

(6) The oxidative curing alkyd-modified silicone acrylic copolymer as described in any one of the above (1) to (5), wherein the silicone (b) further has a phenyl group.

(7) A method for producing an oxidative curing alkyd-modified silicone acrylic copolymer includes the steps of: obtaining an oxidative curing acrylic copolymer (a) by graft polymerizing monomers illustrated in following (a-1), (a-2), and (a-3) into an alkyd resin (c) having an oxidative polymerizable group; and reacting the obtained oxidative curing acrylic copolymer (a) and a silicone (b) having at least one of a hydroxyl group and an alkoxy group. 8 to 40% by mass of the alkyd resin (c), 10 to 30% by mass of the styrenes (a-1), and 5 to 15% by mass of the silicone (b) are used in a total amount of the alkyd resin (c), the styrenes (a-1), the (meth)acrylic acid ester (a-2), the polymerizable unsaturated monomer (a-3), and the silicone (b).

(a-1) styrenes;

(a-2) (meth)acrylic acid ester; and

(a-3) a polymerizable unsaturated monomer having at least one of functional group selected from the group consisting of a hydroxyl group, a carboxyl group, a

glycidyl group, and an isocyanate group.

EFFECT OF THE INVENTION

[0016]

The oxidative curing alkyd-modified silicone acrylic copolymer of the present invention contains the alkyd resin (c), the styrenes (a-1), and the silicone (b) in their respective predetermined proportions. Therefore, the use of the oxidative curing alkyd-modified silicone acrylic copolymer as a coating film forming ingredient makes it possible to produce a coating film that has high initial gloss and satisfies weather resistance, initial drying properties, and impact resistance (strength).

MODE FOR CARRYING OUT THE INVETNION

[0017]

An oxidative curing alkyd-modified silicone acrylic copolymer according to the present invention (hereinafter generally referred to simply as "a copolymer of the present invention") is obtained by reacting an oxidative curing acrylic copolymer (a) and a silicone (b) having at least one of a hydroxyl group and an alkoxy group (hereinafter generally referred to simply as "a silicone (b)").

[0018]

(Oxidative Curing Acrylic Copolymer (a))

The oxidative curing acrylic copolymer (a) used in the present invention is obtained by graft polymerizing monomers illustrated in the following (a-1), (a-2), and

(a-3) into an alkyd resin (c) having an oxidative polymerizable group.

(a-1) styrenes;

(a-2) a (meth)acrylic acid ester; and

(a-3) a polymerizable unsaturated monomer having at least a kind of functional group selected from the group consisting of a hydroxyl group, a carboxyl group, a glycidyl group, and an isocyanate group (hereinafter generally referred to simply as "a polymerizable unsaturated monomer").

[0019]

<Alkyd Resin Having an Oxidative Polymerizable Group (c)>

An alkyd resin is a kind of polyester resins and obtained by condensation of a polyalcohol and a polybasic acid. The present invention employs an alkyd resin (c) having an oxidative polymerizable group among alkyd resins (hereinafter generally referred to simply as "an alkyd resin (c)).

[0020]

The oxidative polymerizable group included in the alkyd resin (c) is, for example, an unsaturated carbon bond derived from an unsaturated fatty acid (carbon-carbon double bond or carbon-carbon triple bond). That is, the alkyd resin (c) is obtained by introducing an unsaturated fatty acid into an alkyd resin. The unsaturated fatty acid is not particularly limited as long as being a fatty acid having at least one

unsaturated carbon bond in a molecule. The unsaturated fatty acid used in the present invention preferably has a somewhat high solid iodine value (namely, has a large number of unsaturated carbon bonds). Examples of the unsaturated fatty acid include drying oil fatty acids and semi-drying oil fatty acids. Although the drying oil fatty acids and the semi-drying oil fatty acids cannot be strictly distinguished, usually, the drying oil fatty acids are unsaturated fatty acids having a solid iodine value of 130 or more, and the semi-drying oil fatty acids are unsaturated fatty acids having a solid iodine value of 100 or more and less than 130. Non-drying oil fatty acids are usually fatty acids having a solid iodine value of less than 100.

[0021]

Examples of the drying oil fatty acids and the semi-drying oil fatty acids include fish oil fatty acids, dehydrated castor oil fatty acids, safflower oil fatty acids, linseed oil fatty acids, soybean oil fatty acids, sesame oil fatty acids, poppy seed oil fatty acids, perilla oil fatty acids, hempseed oil fatty acids, grape kernel oil fatty acids, corn oil fatty acids, tall oil fatty acids, sunflower oil fatty acids, cotton seed fatty acids, walnut oil fatty acids, rubber seed oil fatty acids, Haijien fatty acids, oleic acid, linoleic acid, and linolenic acid. These drying oil fatty acids and these semi-drying oil fatty acids may be used together

with, for example, non-drying oil fatty acids (for example, coconut oil fatty acids, hydrogenated coconut oil fatty acids, and palm oil fatty acids), caproic acid, capric acid, lauric acid, myristic acid, palmitic acid, and stearic acid as necessary.

[0022]

In the present invention, oils and fats (glycerides) may be used together with the unsaturated fatty acids, or instead of the unsaturated fatty acids. The oils and fats are those having an unsaturated carbon bond, and examples thereof include drying oils or semi-drying oils, such as fish oils, dehydrated castor oil, safflower oil, linseed oil, soybean oil, sesame oil, poppy seed oil, perilla oil, hempseed oil, grape kernel oil, corn oil, tall oil, sunflower oil, cotton seed oil, walnut oil, and rubber seed oil.

[0023]

An oil length of the alkyd resin (c) is preferably 30 to 70%. The "oil length" in the present description denotes a proportion (% by mass) of a fatty acid or an oil and fat in raw materials of the alkyd resin (c). The oil length is obtained from the following equation.

Oil length (%) = (Mass of fatty acid or oil and fat / Total mass of raw materials of the alkyd resin (c)) × 100

As long as the oil length falls within the above range, when an obtained copolymer is used as a coating

film forming ingredient, it is possible to obtain a coating film having excellent oxidative curing properties, high crosslink density, high initial gloss, and excellent weather resistance and initial drying properties. Furthermore, a hydrocarbon group derived from the fatty acid and the oil and fat is suitably introduced into molecules of the alkyd resin (c), and hence the solubility into the solvent is further improved during preparation of a coating composition. The oil length is more preferably 40 to 60%.

[0024]

The alkyd resin (c) is obtained by subjecting a polyalcohol and a polybasic acid and an unsaturated fatty acid (or oil and fat) to a condensation reaction (or transesterification reaction). Examples of the polyalcohol include ethylene glycol, diethylene glycol, glycerin, pentaerythritol, mannitol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, hexanediol, trimethylolpropane, dipentaerythritol, and D-sorbitol. Examples of the polybasic acid include phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, succinic acid, succinic anhydride, maleic acid, maleic anhydride, adipic acid, sebacic acid, and tetrahydrophthalic anhydride. A monobasic acid, such as benzoic acid, tert-butylbenzoic acid, hexahydrobenzoic acid, or cinnamic acid, may also be used together as necessary.

[0025]

These raw materials may be usually mixed together and reacted at 170 to 280°C under ordinary pressure or under pressure for 3 to 15 hours. During the reaction, a solvent may be used. For example, xylene, toluene, or methyl isobutyl ketone is usable as the solvent. Other usable solvents are described later. Thus, the alkyd resin (c) having an unsaturated fatty acid residue introduced into the molecule is obtained. Additionally, any well-known catalyst may be used as necessary.

[0026]

The oxidative curing acrylic copolymer (a) used in the present invention is obtained by graft polymerizing the monomers presented in the foregoing (a-1), (a-2), and (a-3) into the alkyd resin (c).

[0027]

<Styrenes (a-1)>

The styrenes (a-1) are used to improve the initial gloss of the coating film. The styrenes (a-1) used in the present invention are not particularly limited, and examples thereof include styrene, α-methyl styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, and p-tert-butylstyrene. Among others, styrene is preferable from an economic point of view and for reasons of availability. These styrenes (a-1) may be used alone, or may be used in combination of two or more kinds. The styrenes (a-1) are preferably used in a proportion of 13

to 40% by mass in a total amount of the foregoing (a-1), (a-2), and (a-3). Generally, the use of a large amount of the styrenes (a-1) tends to deteriorate impact resistance (strength) and weather resistance. Although setting is made so that the amount of the styrenes (a-1) used is relatively large in the present invention, the initial gloss and initial drying properties of the coating film can be further enhanced while hardly deteriorating impact resistance (strength) and weather resistance, owing to balance with other monomers ((a-2) and (a-3)), and balance with the alkyd resin (c) and the silicone (b) to be described later. The styrenes (a-1) are more preferably used in a proportion of 20 to 33% by mass.

[0028]

<(Meth)acrylic Acid Ester (a-2)>

The (meth)acrylic acid ester (a-2) is used for imparting flexibility and weather resistance to the coating film. In the present description, "(meth)acryl" means "acryl" or "methacryl." The (meth)acrylic acid ester (a-2) used in the present invention is not particularly limited, and examples thereof include (meth)acrylic acid alkyls having an alkyl group having 1 to 18 carbon atoms. Examples of the (meth)acrylic acid ester include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl

(meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, and dialkylaminoalkyl (meth)acrylate (for example, dimethylaminoethyl (meth)acrylilate, and diethylaminoethyl (meth)acrylate).

[0029]

As the (meth)acrylic acid ester (a-2), a (meth)acrylic acid ester containing fluorine atoms in a molecule may be used. Examples of the (meth)acrylic acid ester include (meth)acrylic acid esters having 3 to 17 fluorine atoms in a molecule. The (meth)acrylic acid esters having fluorine atoms in a molecule are commercially available from, for example, Osaka Organic Chemical Industry Co., Ltd. under the following product names:

Viscoat 3F (an acrylic acid ester monomer containing 3 fluorine atoms);

Viscoat 4F (an acrylic acid ester monomer containing 4 fluorine atoms);

Viscoat 8F (an acrylic acid ester monomer containing 8 fluorine atoms);

Viscoat 12F (an acrylic acid ester monomer containing 12 fluorine atoms); and

Viscoat 17F (an acrylic acid ester monomer containing 17 fluorine atoms)

Among others, n-butyl acrylate, i-butyl

methacrylate, and t-butyl methacrylate are preferable. These (meth)acrylic acid esters (a-2) may be used alone or in combination of two or more kinds.

[0030]

In general, compounds classified into the (meth)acrylic acid esters may be overlapped with compounds classified into polymerizable unsaturated monomers (a-3) described later. For example, hydroxyethyl (meth)acrylate is classified into (meth)acrylic acid ester and a polymerizable unsaturated monomer. The (meth)acrylic acid ester having a polar functional group is classified into "polymerizable unsaturated monomer (a-3)" in the present description. Examples of the polar functional group include a hydroxyl group, a carboxyl group, a glycidyl group, and an isocyanate group.

[0031]

The (meth)acrylic acid ester (a-2) is preferably used in a proportion of 53-86% by mass in a total amount of the foregoing (a-1), (a-2), and (a-3). By using the (meth)acrylic acid ester (a-2) in the above proportion, the flexibility and weather resistance of the coating film can be further enhanced while hardly deteriorating the initial gloss and impact resistance (strength) of the coating film. The (meth)acrylic acid ester (a-2) is more preferably used in a proportion of 64-79% by mass.

[0032]

<Polymerizable Unsaturated Monomer (a-3)>

The polymerizable unsaturated monomer (a-3) is used to introduce silicone (b) described later into a copolymer (namely, to bond the oxidative curing acrylic copolymer (a) and the silicone (b) together). The polymerizable unsaturated monomer (a-3) is not particularly limited as long as being a polymerizable unsaturated monomer having, in a molecule, at least a kind of functional group selected from the group consisting of a hydroxyl group, a carboxyl group, a glycidyl group, and an isocyanate group. Among others, the polymerizable unsaturated monomer having a hydroxyl group or carboxyl group in a molecule is preferable. These polymerizable unsaturated monomers (a-3) may be used alone or in combination of two or more kinds.

[0033]

Examples of the polymerizable unsaturated monomer having a hydroxyl group include hydroxyl group-containing (meth)acrylic esters, such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 1-methyl-2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate. Among others, 2-hydroxyethyl (meth)acrylate is preferable.

[0034]

Examples of the polymerizable unsaturated monomer having a carboxyl group include α,β-unsaturated

carboxylic acids or salts thereof, such as (meth)acrylic acid, itaconic acid, maleic acid, and fumaric acid; and half ester compounds of the hydroxyl group-containing (meth)acrylic acid ester and acid anhydride. Among others, the α,β-unsaturated carboxylic acids are preferable, (meth)acrylic acid is more preferable, and methacrylic acid is still more preferable.

[0035]

Examples of the polymerizable unsaturated monomer having a glycidyl group include glycidyl group-containing (meth)acrylic acid esters, such as glycidyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate glycidyl ether, and allyl glycidyl ether. Among others, glycidyl (meth)acrylate is preferable.

[0036]

Examples of the polymerizable unsaturated monomer having an isocyanate group include isocyanate group-containing (meth)acrylic acid esters, such as isocyanatomethyl (meth)acrylate, 2-isocyanatoethyl (meth)acrylate, 3-isocyanatopropyl (meth)acrylate, 1-methyl-2-isocyanatoethyl (meth)acrylate, 2-isocyanatopropyl (meth)acrylate, and 4-isocyanatobutyl (meth)acrylate. Among others, 2-isocyanatoethyl (meth)acrylate is preferable.

[0037]

The polymerizable unsaturated monomer (a-3) is preferably used in a proportion of 1 to 7% by mass in a

total amount of the foregoing (a-1), (a-2), and (a-3). By using the polymerizable unsaturated monomer (a-3) in the above proportion, a reaction with the silicone (b) proceeds suitably. It is therefore possible to further enhance the weather resistance and impact resistance (strength) of the coating film while hardly deteriorating the initial gloss of the coating film. In addition, the viscosity of the coating composition is not too high. The polymerizable unsaturated monomer (a-3) is more preferably used in a proportion of 1 to 3% by mass.

[0038]

A method for graft polymerizing these (a-1), (a-2), and (a-3) into the alkyd resin (c) is not particularly limited. For example, in an inert gas atmosphere of nitrogen gas, argon gas, or the like, the polymerization may be carried out by light irradiation or by using a polymerization initiator described below. A reaction temperature is usually 50 to 150°C, and reaction time is usually 3 to 20 hours. More specifically, there is, for example, a method of dropping a mixture of a monomer and a polymerization initiator into a reaction vessel putting the alkyd resin, a method of dropping, into a reaction vessel putting the alkyd resin and part of a monomer, the rest of the monomer and a polymerization initiator, a method of dropping a polymerization initiator into a reaction vessel putting the alkyd resin and a monomer, and a method of dropping the alkyd resin and a

polymerization initiator into a reaction vessel putting a monomer.

[0039]

The polymerization initiator is not particularly limited and is suitably selectable according to the kind of the monomer and reaction conditions. Specific examples thereof include radical polymerization initiators and photo-polymerization initiators. These polymerization initiators may be used alone or in combination of two or more kinds.

[0040]

Examples of the radical polymerization initiators include azo-type compounds, peroxide-type compounds, sulfides, sulfins, sulfinic acids, diazo compounds, and redox-type compounds. Among others, the azo-type compounds or the peroxide-type compounds are preferable.

[0041]

Examples of the azo-type compounds include azobisisobutyronitrile, azobisdimethylvaleronitrile, azobiscyclohexane nitrile, 1,1'-azobis(1-acetoxy-1-phenylethane), dimethyl 2,2'-azobisisobutyrate, and 4,4'-azobis-4-cyanovaleric acid.

[0042]

Examples of the peroxide-type compounds include organic peroxides, such as benzoyl peroxide, lauroyl peroxide, acetyl peroxide, caprylyl peroxide, 2,4-dichlorobenzoyl peroxide, isobutyl peroxide,

acetylcyclohexylsulfonyl peroxide, t-butylperoxypivalate, t-butylperoxy-2-ethylhexanoate, 1,1-di-t-butylperoxy cyclohexane, 1,1-di-t-butylperoxy-3,3,5-trimethyl cyclohexane, 1,1-di-t-hexylperoxy-3,3,5-trimethylcyclohexane, isopropyl peroxydicarbonate, isobutylperoxydicarbonate, s-butylperoxydicarbonate, n-butylperoxydicarbonate, 2-ethylhexylperoxydicarbonate, bis(4-t-butylcyclohexyl) peroxydicarbonate, t-amylperoxy-2-ethylhexanoate, 1,1,3,3-tetramethylbutylperoxy-ethylhexanoate, 1,1,2-trimethylpropylperoxy-2-ethylhexanoate, t-butylperoxyisopropyl monocarbonate, t-amylperoxyisopropyl monocarbonate, t-butylperoxy-2-ethylhexyl carbonate, t-butylperoxyallyl carbonate, t-butylperoxyisopropyl carbonate, 1,1,3,3-tetramethylbutylperoxyisopropyl monocarbonate, 1,1,2-trimethylpropylperoxyisopropyl monocarbonate, 1,1,3,3-tetramethylbutylperoxy isononanoate, 1,1,2-trimethylpropylperoxy-isononanoate, t-butyl peroxybenzoate, t-hexylperoxyisopropyl monocarbonate, and t-amylperoxy-3,5,5-trimethylhexanoate.

[0043]

Examples of the photopolymerization initiator include 2,2-dimethoxy-1,2-diphenylethane-1-one, 1-hydroxycyclohexylphenylketone, 1-cyclohexylphenylketone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-

one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide, and 4-methylbenzophenone.

[0044]

The alkyd resin (c) and a mixture of the above (a-1), (a-2), and (a-3) may be mixed together so that the alkyd resin (c) and the styrenes (a-1) have their respective proportions contained in a copolymer of the present invention described later.

[0045]

Furthermore, monomers other than the above (a-1) to (a-3) may be polymerized into the alkyd resin (c) as long as the effects of the present invention are not impaired. Examples of the monomers other than the above (a-1) to (a-3) include (meth)acrylonitrile, (meth)acrylamide, vinyl acetate, vinyl chloride, vinylpyrrolidone, vinyloxazoline, and acryloylmorpholine. The monomers other than the above (a-1) to (a-3) are contained in a proportion of 5% by mass or less, preferably 2% by mass or less in total in the oxidative curing alkyd-modified silicone acrylic copolymer.

[0046]

The mixture of the above (a-1), (a-2), and (a-3) can be graft polymerized into the alkyd resin (c) by the above method. The impact resistance (strength), weather resistance, initial gloss, and initial drying properties

of the coating film can be improved by graft polymerizing the mixture of the above (a-1), (a-2), and (a-3) into the alkyd resin.

[0047]

(Silicone (b) having at least one of a hydroxyl group and an alkoxy group)

The silicone (b) used in the present invention is, for example, polysiloxane having a branched structure whose main chain is a siloxane bond (-Si-O-Si-) and whose side chains are respectively substituent groups, such as an alkyl group, an aryl group, a hydroxyl group, and an alkoxy group. The silicone (b) is not particularly limited as long as being silicone having at least one of the hydroxyl group and the alkoxy group.

[0048]

At least one of the hydroxyl group and the alkoxy group is preferably directly bonded to at least one silicon atom in a silicone molecule.

[0049]

The silicone (b) is, for example, illustrated by the formula: $R^1_m (R^2O)_n SiO_{(4-m-n)/2}$.

(In the formula, R^1 and R^2 are the same or different and are a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, or an aryl group having 6 to 12 carbon atoms, m satisfies $0 \leq m \leq 3.5$, and n satisfies $0.0005 \leq n < 4$). The silicone (c) is a mixture of molecules that are different in degree of polymerization and in degree of substitution

of a functional group. Therefore, the values of m and n in the above formula are not necessarily an integer.

[0050]

Examples of the alkyl group having 1 to 8 carbon atoms include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, and a tert-butyl group. Among others, an alkyl group having 1 to 3 carbon atoms is preferable for imparting weather resistance to the coating film. A propyl group (n-propyl group or isopropyl group) is more preferable in view of solubility into a solvent. When the carbon number is 3 or more, a cyclic alkyl group may be employed.

[0051]

Examples of the aryl group having 6 to 12 carbon atoms include a phenyl group, a benzyl group, a tolyl group, a xylyl group, and a naphthyl group. Among others, an aryl group having 6 to 8 carbon atoms is preferable, and the phenyl group is more preferable.

[0052]

The silicone (b) is preferably a silicone further having a phenyl group in addition to the hydroxyl group or alkoxy group, and the phenyl group is more preferably directly bonded to a silicon atom. The use of the silicone having the phenyl group makes it possible to further enhance the solubility into a solvent (particularly, a weak solvent described later).

Consequently, it is possible to appropriately reduce the viscosity of a coating material, thus further improving working efficiency. Additionally, the refractive index of the coating film is improved to improve the initial gloss. A silicone having an alkyl group is preferable, and the alkyl group is more preferably directly bonded to a silicon atom. A silicone having a phenyl group directly bonded to a silicon atom, and a propyl group directly bonded to a silicon atom (an n-propyl group or an isopropyl group) is particularly preferable. The silicone having the phenyl group and the propyl group respectively bonded to the silicon atom is generally referred to as "a phenylpropyl-type silicone," but a phenylpropyl group is not bonded to the silicon atom. Similarly, "a phenylmethyl-type silicone" exists, but a phenylmethyl group is not bonded to the silicon atom. Here, the silicone denotes the silicone having the phenyl group and the propyl group respectively bonded to the silicon atom.

[0053]

A molecular weight of the silicone (b) is not particularly limited. The present invention preferably employs a silicone having a number average molecular weight of 200 to 5,500, more preferably a silicone having a number average molecular weight of 1,400 to 3,000.

As representative commercially available products of these silicones, there are, for example, 3037

INTERMEDIATE, 3074 INTERMEDIATE, Z-6018, 217 FLAKE, 220 FLAKE, 233 FLAKE, 249 FLAKE, QP8-5314, SR2402, and AY 42-163 (all of which are produced by Dow Corning Toray Co., Ltd.); TSR160, TSR165, and TSR3168 (all of which are produced by Momentive Performance Materials Inc.); KR-211, KR-216, KR-213, and KR-9218 (all of which are produced by Shin-Etsu Chemical Co., Ltd.); and SILRES SY 231, SILRES SY 300, SILRES SY 409, and SILRES IC368 made (all of which are produced by Wacker Asahi Kasei Silicone Co., Ltd.).

[0054]

(Oxidative Curing Alkyd-Modified Silicone Acrylic Copolymer)

The copolymer of the present invention has a characteristic feature that the alkyd resin (c), the styrenes (a-1), and the silicone (b) are polymerized in their respective particular proportions. That is, 8 to 40% by mass of the alkyd resin (c), 10 to 30% by mass of the styrenes (a-1), and 5 to 15% by mass of the silicone (b) are contained in a total amount of the alkyd resin (c), the styrenes (a-1), the (meth)acrylic acid ester (a-2), the polymeraizable unsaturated monomer (a-3), and the silicone (b).

[0055]

When the content of the alkyd resin (c) is less than 8% by mass, there occurs a decrease in oxidative polymerizable portion. Accordingly, an obtained coating

film has low solvent resistance, and the coating film has poor weather resistance, poor initial drying properties, and poor apparent thickness. When the content of the alkyd resin (c) exceeds 40% by mass, gelling is apt to occur during production of a copolymer. Even when the gelling does not occur, the coating film using the copolymer is subject to deterioration in water resistance, alkali resistance, and weather resistance. The alkyd resin (c) is preferably contained in a proportion of 15 to 25% by mass.

[0056]

When a content of the styrenes (a-1) is less than 10% by mass, the coating film is subject to deterioration in initial gloss and initial drying properties. When the content of the styrenes (a-1) exceeds 30% by mass, the coating film has poor impact resistance (strength) and is subject to a considerable deterioration in weather resistance. The styrenes (a-1) is preferably contained in a proportion of 15 to 25% by mass.

[0057]

When a content of the silicone (b) is less than 5% by mass, the coating film is subject to a considerable deterioration in weather resistance. When the content of the silicone (b) exceeds 15% by mass, gelling is apt to occur during production of a copolymer. Even when the gelling does not occur, the coating film using the copolymer has poor impact resistance (strength) and poor

apparent thickness. The silicone (b) is preferably contained in a proportion of 7 to 12% by mass.

[0058]

The styrenes (a-1), the (meth)acrylic acid ester (a-2), and the polymerizable unsaturated monomer (a-3) are preferably contained in a proportion of 45 to 87% by mass, more preferably 63 to 78% by mass in total in the copolymer of the present invention.

[0059]

The copolymer of the present invention preferably has a solid iodine value of 5 to 50. When the solid iodine value falls within the above range, an obtained coating film has satisfactory water resistance and alkali resistance in addition to weather resistance, and also has satisfactory strength and apparent thickness. Furthermore, gelling is less apt to occur during the production of the copolymer, and the solubility into the weak solvent is less apt to deteriorate. The copolymer of the present invention more preferably has a solid iodine value of 18 to 46, still more preferably 20 to 40. The solid iodine value is measurable according to JIS K0070 (Test method for acid value, saponification value, ester value, iodine value, hydroxy value, and unsaponifiable matter of chemical products).

[0060]

A weight average molecular weight of the copolymer of the present invention is not particularly limited.

The copolymer of the present invention preferably has a weight average molecular weight of 10,000 to 150,000. When the weight average molecular weight falls within the above range, an obtained coating film has satisfactory water resistance and alkali resistance in addition to weather resistance, and also has higher initial gloss. Additionally, viscosity of a coating material is not too high, and working efficiency during a coating process is further enhanced. The weight average molecular weight of the copolymer of the present invention is more preferably 30,000 to 100,000, still more preferably 40,000 to 80,000. The weight average molecular weight is measured, for example, by gel permeation chromatography (GPC).

[0061]

(Method for Producing Oxidative Curing Alkyd-Modified Silicone Acrylic Copolymer)

The copolymer of the present invention is obtained by reacting, for example, the oxidative curing acrylic copolymer (a) and the silicone (b) as described above. That is, functional groups existing in the oxidative curing acrylic copolymer (a) (at least one kind selected from the group consisting of a hydroxyl group, a carboxyl group, a glycidyl group, and an isocyanate group), and a hydroxyl group or an alkoxy group existing in the silicone (b) are bonded together by dehydration or dealcoholization condensation, thus resulting in the oxidative curing alkyd-modified silicone acrylic

copolymer of the present invention.

[0062]

The dehydration or dealcoholization condensation reaction of the oxidative curing acrylic copolymer (a) and the silicone (b) is carried out for 2 to 8 hours by, for example, mixing the oxidative curing acrylic copolymer (a) and the silicone (b), and then heating this to 130 to 180°C while removing water or alcohol to be produced. The reaction may be further carried out under the presence of known catalyst and reflux solvent as necessary. The dehydration or dealcoholization condensation reaction of the oxidative curing acrylic copolymer (a) and the silicone (b) contributes to improving the weather resistance of the coating film. Meanwhile, the weather resistance of the coating film becomes insufficient only by mixing the oxidative curing acrylic copolymer (a) and the silicone (b) without reaction therebetween (cold blend).

[0063]

An organic solvent may be used as necessary in the process of producing each of the alkyd resin (c), and the oxidative curing acrylic copolymer (a), or the copolymer of the present invention. Examples of usable organic solvents include mineral spirits (also known as mineral turpentine or white spirit), isoparaffin, hexane, heptane, octane, nonane, decane, cyclohexane, cycloheptane, toluene, xylene, ethyl acetate, butyl acetate, methanol,

ethanol, butanol, propanol, methyl ethyl ketone, and methyl isobutyl ketone. These solvents may be used alone or in combination of two or more kinds.

[0064]

It is preferable to use a weak solvent in consideration of environment and painting workers' health. The weak solvent denotes an aliphatic hydrocarbon solvent that may contain a high boiling aromatic hydrocarbon solvent, namely, that has a high flash point, a high-boiling point, and low harmfulness as typically represented by turpentine and mineral spirits. Examples of mixed solvents include mineral spirits, white spirit, mineral turpentine, isoparaffin, solvent kerosene, aromatic naphtha, VM & P naphtha, and solvent naphtha. Examples of single-component solvents include aliphatic hydrocarbons, such as n-butane, n-hexane, n-heptane, n-octane, isononane, n-decane, n-dodecane, cyclopentane, cyclohexane, and cyclobutane.

[0065]

The copolymer of the present invention thus obtained contains the alkyd resin (c), the styrenes (a-1), and the silicone (b) in their respective predetermined proportions. Therefore, the use of the copolymer as a coating film forming ingredient makes it possible to obtain the coating film having high initial gloss and satisfactory weather resistance, initial drying properties, and impact resistance (strength). Hence, the

copolymer of the present invention is suitably usable as, for example, a coating film forming ingredient and binder in various kinds of coating compositions (for example, intended for buildings (indoor painting and outdoor painting), automobiles, and baking), and in ink compositions. The coating composition is prepared by mixing the copolymer of the present invention with, depending on the application, a solvent, a pigment, and a dryer, and further, other additives (a leveling agent and a dripping-preventing agent) as necessary.

[0066]

As the solvent, it is possible to use the same one that is used as necessary in the process of producing the alkyd resin (c), the oxidative curing acrylic copolymer (a), or the copolymer of the present invention. Examples of the pigment include inorganic pigments, such as titanium dioxide, carbon black, calcium oxide, barium sulfate, silica, clay, talc, and silica sand, and organic pigments, such as phthalocyanine blue. Examples of the dryer include cobalt salt, manganese salt, lead salt, zirconium salt, and calcium salt of naphthenic acid or octyl acid.

[0067]

Approximately 10 to 90% by mass, preferably approximately 40 to 70% by mass of the copolymer of the present invention is contained in the coating composition. An obtained coating composition is usable as a room

temperature curable coating composition, a baking type coating composition, or the like.

[EXAMPLES]

[0068]

The present invention is specifically illustrated below by examples and comparative examples, but the present invention is not limited to these examples.

[0069]

(Synthesis Example: Synthesis of Alkyd Resin)

The following raw materials were loaded into a reaction vessel and reacted until reaching an acid value of 5 or less, by raising temperature to 240°C while removing water in a reaction system by a water separator. Xylene was removed by a vacuum distillation at a point in time that the acid value reached 5 or less. After cooling, an obtained reaction product was diluted with 350 parts by mass of mineral spirits, thereby obtaining an alkyd resin having an oil length of 50%, an acid value of 2.5, viscosity of Z (Gardner bubble viscometer/25°C), a color number of 6 (Gardner), and a nonvolatile content of 60% by mass.

phthalic anhydride: 140 parts by mass;

dehydrated castor oil fatty acid: 260 parts by mass;

glycerin: 50 parts by mass;

pentaerythritol: 70 parts by mass; and

reflux solvent (xylene): 15.6 parts by mass

[0070]

(Example 1)

<Synthesis of Oxidative Curing Alkyd-Modified Silicone Acrylic Resin (Copolymer)>

First, 17.53 parts by mass of the alkyd resin (nonvolatile content 60% by mass) obtained in the above synthesis example, and 31.78 parts by mass of mineral spirits were loaded into a reaction vessel. This was heated to 120°C while stirring and allowing nitrogen gas to pass through. Then, the following mixture was dropped in the reaction vessel for 2 hours while being held at 120°C. A proportion in the following parentheses indicates a proportion of each monomer when a total amount of monomers is 100% by mass.

(Mixture)

i-butyl methacrylate: 21.24 parts by mass (50.0% by mass);

t-butyl methacrylate: 2.12 parts by (5.0% by mass);

n-butyl acrylate: 7.95 parts by weight (18.7% by mass);

styrene: 10.70 parts by mass (25.2% by mass);

2-hydroxyethyl methacrylate: 0.43 parts by mass (1.0% by mass);

methacrylic acid: 0.04 parts by mass (0.1% by mass); and

t-hexylperoxyisopropyl monocarbonate: 0.46 parts by mass

[0071]

After completion of the dropping, this was reacted for 4 hours at 120°C, and a water separator was attached to the reaction vessel. Next, 3.96 parts by mass of a silicone resin Z-6018 (a solid resin having a nonvolatile content of 100% by mass and a number average molecular weight of 2,000, and having a phenyl group and a propyl group to be directly bonded to a silicon atom, produced by Dow Corning Toray Co., Ltd.) was added into the reaction vessel and heated to 160°C. A reaction was carried out for 4 hours while removing water in the reaction system by the water separator. After the reaction, this was cooled to 80°C, and 3.79 parts by mass of mineral spirits was added into the reaction vessel, thereby obtaining a brown clear viscous oxidative curing alkyd-modified silicone acrylic copolymer (resin) (having a non-volatile content of 55% by mass).

[0072]

A weight average molecular weight of the resultant resin was measured by gel permeation chromatography (GPC). The resin was dissolved in tetrahydrofuran (having a concentration of 1.0 g/L), and a measurement was made by the GPC with a differential refractive index detector (RID), thereby obtaining a molecular weight distribution of the resin. Thereafter, a weight average molecular weight of the resin (Mw) was calculated from an obtained chromatogram (chart) by using a standard polystyrene as a

calibration curve. The weight average molecular weight of the resultant resin was 44,000. Measuring devices and measuring conditions were as follows.

Data processer: HLC-8220GPC (manufactured by Tosoh Corporation);

Differential refractive index detector: RI detector included in HLC-8220GPC;

Column: Two columns of TSKgel SuperHZM-H (manufactured by Tosoh Corporation);

Mobile phase: tetrahydrofuran;

Column flow rate: 0.35 mL/min;

Sample concentration: 1.0 g/L;

Loading amount: 10 μL;

Measurement temperature: 40°C; and

Molecular weight marker: standard polystyrene (standard substance produced by POLYMER LABORATORIES Co., Ltd.) (using POLYSTYRENE-MEDIUM MOLECULAR WEIGHT CALIBRATION KIT)

[0073]

A solid iodine value of the resultant resin was measured according to JIS K0070 (Test method for acid value, saponification value, ester value, iodine value, hydroxy value, and unsaponifiable matter of chemical products).

[0074]

<Preparation of Coating Composition>

57.0 parts by mass of the resultant resin (having a

nonvolatile content of 55% by mass), 23.5 parts by mass of mineral spirits as a solvent, 14.0 parts by mass of titanium oxide JR-603 (produced by TAYCA CORPORATION) as a pigment, 3.5 parts by mass of a dryer composed of cobalt octylate and zirconium octylate, and 2.0 parts by mass of a dripping-preventing agent as an additive were added and kneaded by a triple roll mill, thereby preparing a coating composition (ordinary temperature curable coating composition).

[0075]

(Examples 2-18 and Comparative Examples 1-8)

Oxidative curing alkyd-modified silicone acrylic copolymers were respectively obtained in the same procedure as in Example 1 except that ingredients illustrated in Table 1 were respectively used in proportions illustrated in Table 1. Coating compositions were prepared in the same procedure as in Example 1 except for using the resultant resins, respectively. Abbreviations illustrated in Table 1 indicate the following compounds. The meaning of "phenylpropyl-type" and "phenylmethyl-type" of the silicone is as described above.

i-BMA: i-butyl methacrylate;

t-BMA: t-butyl methacrylate;

n-BA: n-butyl acrylate;

St: styrene;

2-HEMA: 2-hydroxyethyl methacrylate; and

MA: methacrylic acid

[0076]

(Evaluations)

The coating compositions obtained in Examples 1 to 18 and Comparative Examples 1 to 8 were evaluated in terms of (1) initial gloss, (2) initial drying properties, (3) accelerated weathering resistance, and (4) impact resistance. The results are presented in Table 2. A determination was made that it lacked practicality as the coating composition when failed to pass the evaluation (when a grade "C" was given) in at least one of these physical properties (1) to (4).

[0077]

(1) Initial Gloss

The resultant coating composition (ordinary-temperature curable coating composition) was coated on a glass plate (150 mm × 70 mm) having a thickness of 3 mm by using a film applicator AP250 (manufactured by Taiyukizai Co., LTD.). The coated glass plate was dried in a room of 23°C and 50% RH for a week, and 20° specular reflectivity (20° G) was measured. A measured value thereof was converted to a specular gloss according to JIS Z8741. An evaluation was made according to the following criteria, and a grade "B" or above (having specular reflectivity of 80 or more) was considered as passing.

A+: when the specular gloss was 90 or more;

A: when the specular gloss was 85 or more and less than 90;

B: when the specular gloss was 80 or more and less than 85; and

C: when the specular gloss was less than 80

[0078]

(2) Initial Drying Properties

A test was carried out with a method obtained by partially changing JIS K 5600-3-6 (Print free test). The resultant coating composition (ordinary temperature curable coating composition), a weight (500 g, and 40 mm in diameter of a bottom surface), a tin plate (300 mm × 70 mm) with a thickness of 0.3 mm, a painting tool (film applicator AP250), and a pharmacopeia gauze (one being usually available from a pharmacy, which was used by being cut into a 50 mm square) were allowed to stand in an atmosphere of 23°C for 24 hours. Then, the resultant coating composition (ordinary temperature curable coating composition) was coated on the tin plate using the film applicator AP250. The coated tin plate was allowed to stand in a room of 23°C and 50% RH for 2 hours. The gauze was placed on a coating film surface, and the weight was placed thereon. The weight was removed after one hour. A state in which the gauze was turned over was evaluated according to the following criteria. A grade "B" or above was considered as passing.

A+: when the gauze was peeled off without

resistance, leaving no trace on the coating film surface;

A: when the gauze was peeled off without resistance although a trace remained on the coating film surface;

B: when resistance occurred during peeling off the gauze; and

C: when the base (tin plate) appeared during peeling off the gauze

[0079]

(3) Accelerated Weathering Properties

The resultant coating composition (ordinary-temperature curable coating composition) was coated on a dull steel plate (150 mm × 70 mm) having a thickness of 0.8 mm by using the film applicator AP250. The coated dull steel plate was dried in a room of 23°C and 50% RH for a week, and a gloss retention (20° GR) after exposure for 1500 hours was found by a Sunshine Weather Meter (manufactured by Suga Test Instruments Co., Ltd.). Then, an evaluation was made according to the following criteria. A grade "B" or above (having gloss retention of 70% or more) was considered as passing. The gloss retention is obtained by the following equation.

Gloss retention (%) = (Specular reflectivity after test / Specular reflectivity before test) × 100

A+: when the gloss retention was 90% or more;

A: when the gloss retention was 80% or more and less than 90%;

B: when the gloss retention was 70% or more and

less than 80%; and

C: when the gloss retention was less than 70%

[0080]

(4) Impact Resistance

A test of impact resistance was carried out according to JIS K 5600-5-3 (Falling-weight test), and an evaluation was made according to the following criteria. A grade "B" or above was considered as passing.

A: when the coating film was not broken under impact of 1 kg × 15 cm;

B: when the coating film was not broken under impact of 1 kg × 10 cm, but was broken under impact of 1 kg × 15 cm; and

C: when the coating film was broken under impact of 1kg × 10 cm

[0081]

[Table 1]

		Monomer compositions being graft polymerized to alkyd resin(*1)						Silicone(*2)				Alkyd resin(*2)	Styrene(*2)	Solid iodine value	Mw
		i-BMA	t-BMA	n-BA	St	2-HEMA	MA	Phenylpropyl-type	Phenylmethyl-type	Phenyl-type	Methyl-type				
		(a−2)			(a−1)	(a−3)		(b)				(c)	(a−1)		
Examples	1	50.0	5.0	18.7	25.2	1.0	0.1	7.0	—	—	—	18.6	18.7	21.0	44000
	2	47.5	5.0	17.2	25.2	5.0	0.1	7.0	—	—	—	18.6	18.7	22.0	58000
	3	61.0	5.4	17.5	14.0	2.0	0.1	7.0	—	—	—	18.6	10.4	21.0	55000
	4	36.3	4.7	17.9	39.0	2.0	0.1	7.0	—	—	—	18.6	29.0	22.0	59000
	5	51.7	5.0	16.0	25.2	2.0	0.1	—	7.0	—	—	18.6	18.7	22.0	58000
	6	51.7	5.0	16.0	25.2	2.0	0.1	—	—	7.0	—	18.6	18.7	22.0	59000
	7	51.7	5.0	16.0	25.2	2.0	0.1	—	—	—	7.0	18.6	18.7	22.0	62000
	8	50.9	5.0	16.8	25.2	2.0	0.1	7.3	—	—	—	15.1	19.6	18.0	50000
	9	50.9	5.0	16.8	25.2	2.0	0.1	6.5	—	—	—	24.9	17.3	29.0	60000
	10	50.9	5.0	16.8	25.2	2.0	0.1	5.3	—	—	—	39.0	14.0	46.0	74000
	11	58.9	6.2	18.0	14.8	2.0	0.1	7.0	—	—	—	18.6	11.0	22.0	49000
	12	53.6	6.2	18.0	20.1	2.0	0.1	7.0	—	—	—	18.6	15.0	22.0	47000
	13	37.1	6.2	21.6	33.0	2.0	0.1	7.0	—	—	—	18.6	24.6	23.0	59000
	14	31.0	6.2	21.8	38.9	2.0	0.1	7.0	—	—	—	18.6	28.9	20.0	57000
	15	51.7	5.0	16.0	25.2	2.0	0.1	5.0	—	—	—	19.0	19.2	22.0	49000
	16	51.7	5.0	16.0	25.2	2.0	0.1	7.0	—	—	—	18.6	18.7	22.0	52000
	17	51.7	5.0	16.0	25.2	2.0	0.1	12.0	—	—	—	17.6	17.7	20.0	60000
	18	51.7	5.0	16.0	25.2	2.0	0.1	15.0	—	—	—	17.0	17.1	19.0	63000
Comparative Examples	1	62.7	6.2	19.0	10.0	2.0	0.1	7.0	—	—	—	18.6	7.4	22.0	50000
	2	28.2	5.0	23.4	41.3	2.0	0.1	7.0	—	—	—	18.6	30.7	22.0	53000
	3	51.0	5.0	16.7	25.2	2.0	0.1	3.0	—	—	—	19.4	19.6	23.0	48000
	4	51.0	5.0	16.7	25.2	2.0	0.1	15.7	—	—	—	16.9	17.0	20.0	61000
	5	51.0	5.0	16.7	25.2	2.0	0.1	8.2	—	—	—	5.3	21.8	6.0	37000
	6	51.0	5.0	16.7	25.2	2.0	0.1	5.1	—	—	—	41.1	13.6	49.0	80000
	7	64.5	5.0	17.6	10.8	2.0	0.1	7.0	—	—	—	18.6	8.0	22.0	54000
	8	13.9	2.1	25.4	56.5	2.0	0.1	7.0	—	—	—	18.6	42.0	22.0	65000

*1 : Values of the monomer compositions being graft polymerized to alkyd resin indicate proportions (% by mass) when a total amount of monomers is 100% by mass.

*2 : Values of silicone, alkyd resin and styrene indicate proportions (% by mass) when solid content of finally obtained copolymer is 100% by mass.

[0082]

[Table 2]

		Intial gross	Initial drying properties	Accelerated weathering resistance	Impact resistance
Examples	1	A	A	A	A
	2	B	A	A	A
	3	B	A	A	A
	4	A+	A	B	B
	5	B	A	A	A
	6	B	A	A	A
	7	B	A	A	A
	8	A	B	A	B
	9	B	A	A	A
	10	B	A	B	A
	11	B	B	A	A
	12	B	B	A	A
	13	A+	A	B	A
	14	A+	A	B	B
	15	A	A	A	A
	16	A	A	A	A
	17	B	A	A+	A
	18	B	B	A+	B
Comparative Examples	1	C	C	A+	A
	2	A+	A+	C	C
	3	B	B	C	A
	4	B	A	A+	C
	5	A	C	C	B
	6	B	A+	C	A
	7	C	C	A	A
	8	A+	A	C	C

[0083]

Table 2 illustrates that in Examples 1 to 18, when the resultant resin was used as a coating film forming ingredient, the resultant coating film has high initial gloss and is also excellent in initial drying properties, weather resistance, and impact resistance (strength).

[0084]

Table 2 also illustrates that Comparative Examples 1 to 8, in which the content of the alkyd resin (c), the styrenes (a-1), or the silicone (b) is outside the range of the present invention, are poor in at least one of initial gloss, initial drying properties, weather resistance, and impact resistance (namely, a grade "C" in initial gloss (having specular gloss of less than 80), a grade "C" in initial drying properties, a grade "C" in weather resistance (having gloss retention of less than 70%), or a grade "C" in impact resistance).

[0085]

(Comparative Example 9)

<Synthesis of Silicone-Modified Acrylic Copolymer>

First, 100 parts by mass of a mineral spirit was loaded into a reaction vessel, and this was heated to 115°C while stirring and allowing nitrogen gas to pass through. Then, the following mixture was dropped in the reaction vessel for 4 hours while keeping at a temperature of 115°C.

(Mixture)

n-butyl methacrylate: 15 parts by mass;

i-butyl methacrylate: 20 parts by mass;

styrene: 25 parts by mass;

2-ethylhexyl acrylate: 20 parts by mass;

glycidyl methacrylate: 20 parts by mass; and

2,2'-azobisisobutyronitrile: 1 part by mass

[0086]

After completion of the dropping, this was reacted for 2 hours at 115°C. Next, 30 parts by mass of linseed oil fatty acid and 0.4 parts by mass of N,N-dimethylaminoethanol as a reaction catalyst were added after raising the temperature to 140°C. An addition reaction of fatty acid was carried out while keeping at a temperature of 160°C for 5 hours. An acid value of a resin was traced by KOH titrimetric method, and a point in time that the acid value of the resin reached 1.0 or less was regarded as a terminal point. After termination of the reaction, a dilution was carried out by adding 45 parts by mass of xylene, thereby obtaining a brown clear viscous fatty acid-modified copolymer solution having a non-volatile content of 47% by mass. This was then cooled to 100°C, and a water separator was attached to the reaction vessel. Next, 15 parts by mass of Z-6018 (a silicone produced by Dow Corning Toray Co., Ltd.), 14 parts by mass of a mineral spirit, 6 parts by mass of xylene, and 0.20 parts by mass of tetra-n-butyltitanate as a reaction catalyst were added into the reaction vessel. This was heated to 165°C, and a reaction was carried out for 5 hours while separating water by the water separator in a reflux system, thereby obtaining a brown clear viscous silicone-modified acrylic copolymer having a non-volatile content of 47% by mass.

[0087]

A proportion of the styrene was 17.2% by mass and a proportion of the silicone was 10.3% by mass in the raw materials of the silicone-modified acrylic copolymer (in terms of solid content). A weight average molecular weight and a solid iodine value of the resultant resin were measured in the same procedure as in Example 1. The weight average molecular weight thereof was 40,000, and the solid iodine value thereof was 28. Using the resultant resin, a coating composition was prepared in the same procedure as in Example 1 except that the amount of the mineral spirit was adjusted so as to have the same nonvolatile content as in Example 1. The obtained coating composition was evaluated in terms of (1) initial gloss, (2) initial drying properties, (3) accelerated weathering resistance, and (4) impact resistance as described above. The results thereof are presented in Table 3.

[0088]

(Comparative Example 10)

<Synthesis of Alkyd Resin>

The following raw materials were loaded into a reaction vessel and were reacted until reaching an acid value of 8 or less, by raising temperature to 240°C while removing water in a reaction system by a water separator. Xylene was removed by a vacuum distillation at a point in time that the acid value reached 8 or less. After cooling, an obtained reaction product was diluted with

350 parts by mass of a mineral spirit, thereby obtaining an alkyd resin having an oil length of 50%, an acid value of 5.5, viscosity of Z (Gardner bubble viscometer / 25°C), a color number of 6 (Gardner), and a nonvolatile content of 58% by mass.

phthalic anhydride: 140 parts by mass;

dehydrated castor oil fatty acid: 260 parts by mass;

glycerin: 50 parts by mass;

pentaerythritol: 70 parts by mass; and

reflux solvent (xylene): 15.6 parts by mass

[0089]

In Comparative Example 9, it was attempted to carry out a reaction using 30 parts by mass of the alkyd resin obtained above instead of 30 parts by mass of linseed oil fatty acid. However, the reaction did not proceed (an acid value of the resin did not decline). Therefore, the reaction was canceled, and no evaluation was made.

[0090]

(Comparative Example 11)

An evaluation of a coating composition was made using a resin in which none of the monomers indicated in the above (a-1) to (a-3), such as the styrenes, were not graft polymerized into the alkyd resin.

<Synthesis of Acrylic Resin (Copolymer)>

First, 42.41 parts by mass of a mineral spirit was loaded into a reaction vessel, and this was heated to

118°C while stirring and allowing nitrogen gas to pass through. Then, the following mixture was dropped in the reaction vessel for 3 hours while keeping at a temperature of 118°C. A ratio in the following parentheses indicates a proportion of each monomer when a total amount of monomers is 100% by mass.

(Mixture)

i-butyl methacrylate: 28.51 parts by mass (50.0% by mass);

t-butyl methacrylate: 2.85 parts by (5.0% by mass);

n-butyl acrylate: 10.67 parts by weight (18.7% by mass);

styrene: 14.36 parts by mass (25.2% by mass);

2-hydroxyethyl methacrylate: 0.57 parts by mass (1.0% by mass);

methacrylic acid: 0.05 parts by mass (0.1% by mass); and

t-hexylperoxyisopropyl monocarbonate: 0.58 parts by mass

[0091]

After completion of the dropping, this was reacted for 4 hours at 120°C and then cooled to 80°C, thereby obtaining a brown clear viscous acrylic copolymer having a non-volatile content of 57% by mass.

[0092]

<Reaction of Alkyd Resin, Copolymer, and Silicone Resin>

First, 17.60 parts by mass of the alkyd resin

(having a non-volatile content of 60% by mass) used in Example 1, 74.81 parts by mass of the acrylic copolymer (having a non-volatile content of 57% by mass), 3.98 parts by mass of the silicone resin (Z-6018) used in Example 1, and 7.58 parts by mass of a mineral spirit were loaded into a reaction vessel having a water separator attached thereto. This was then stirred at 120°C for 4 hours while allowing nitrogen gas to pass through, thereby obtaining a resin (having a non-volatile content of 55% by mass). A proportion of the styrene was 18.8% by mass, a proportion of the alkyd resin was 18.5% by mass, and a proportion of the silicone was 7.0% by mass in terms of solid content, all of which constituted the resultant resin. A weight average molecular weight and a solid iodine value of the resultant resin were measured in the same procedure as in Example 1. The weight average molecular weight was 47,000, and the solid iodine value was 21.

[0093]

A coating composition was prepared using the resultant resin in the same procedure as in Example 1. The obtained coating composition was evaluated in terms of (1) initial gloss, (2) initial drying properties, (3) accelerated weathering resistance, and (4) impact resistance as described above. The results are presented in Table 3.

[0094]

(Comparative Example 12)

An evaluation of a coating composition was made using a mixture obtained by merely mixing (cold blending) the oxidative curing acrylic copolymer (a) and the silicone (b) without reaction therebetween. Firstly, 17.53 parts by mass of the alkyd resin (having a non-volatile content of 60% by mass) used in Example 1, and 31.78 parts by mass of a mineral spirit were loaded into a reaction vessel. This was heated to 120°C while stirring and allowing nitrogen gas to pass through. Then, the following mixture was dropped for 2 hours while keeping at a temperature of 120°C. A proportion in the following parentheses indicates a proportion of each monomer when a total amount of monomers is 100% by mass.

(Mixture)

i-butyl methacrylate: 21.24 parts by mass (50.0% by mass);

t-butyl methacrylate: 2.12 parts by (5.0% by mass);

n-butyl acrylate: 7.95 parts by weight (18.7% by mass);

styrene: 10.70 parts by mass (25.2% by mass);

2-hydroxyethyl methacrylate: 0.43 parts by mass (1.0% by mass);

methacrylic acid: 0.04 parts by mass (0.1% by mass); and

t-hexylperoxyisopropyl monocarbonate: 0.46 parts by mass

[0095]

After completion of the reaction, this was reacted for 4 hours at 120°C to obtain an oxidative curing acrylic copolymer (a graft polymer of the monomers into the alkyd resin). Then, a water separator was attached to the reaction vessel, and the copolymer was cooled to 80°C. The silicone resin (Z-6018) used in Example 1 was loaded therein and stirred at 80°C for 2 hours. In this period, no water was generated in the reaction system. Then, 3.79 parts by mass of a mineral spirit was loaded into the reaction vessel, thereby obtaining a brown clear viscous mixture of the oxidative curing acrylic copolymer (the graft polymer of the monomers into the alkyd resin) and the silicone. A proportion of the styrene was 18.7% by mass, a proportion of the alkyd resin was 18.6% by mass, and a proportion of the silicone was 7.0% by mass in terms of solid content, all of which were contained in the obtained mixture. A weight average molecular weight and a solid iodine value of the obtained mixture were measured in the same procedure as in Example 1. The weight average molecular weight was 40,000, and the solid iodine value was 22.

[0096]

A coating composition was prepared using the obtained mixture in the same procedure as in Example 1. The obtained coating composition was evaluated in terms of (1) initial gloss, (2) initial drying properties, (3)

accelerated weathering resistance, and (4) impact resistance as described above. The results are presented in Table 3.

[0097]

[Table 3]

		Intial gross	Initial drying properties	Accelerated weathering resistance	Impact resistance
Comparative Examples	9	C	A	A	B
	10	—	—	—	—
	11	C	C	C	C
	12	A	A	C	B

[0098]

The table 3 illustrates the following. That is, Comparative Example 9 containing no alkyd resin has poor initial gloss. Comparative Example 10 used the alkyd resin instead of the unsaturated fatty acid (linseed oil fatty acid) in Comparative Example 9. However, the reaction of the epoxy group-containing vinyl copolymer and the alkyd resin did not proceed, failing to obtain a resin. Comparative Example 11 used the resin in which the monomers indicated in the above (a-1) to (a-3), such as the styrenes, were not graft polymerized into the alkyd resin. However, the crosslinking reaction during the formation of the coating film was less apt to proceed, thus being poor in all of initial gloss, initial drying properties, weather resistance, and impact resistance. Comparative Example 12 used the mixture obtained merely by mixing (cold blending) the oxidative curing acrylic

copolymer and the silicone without reaction therebetween. However, Comparative Example 12 had poor weather resistance. This seems because the silicone is not reacted with the oxidative curing acrylic copolymer and the silicone bleeds out over time.

CLAIMS

1. An oxidative curing alkyd-modified silicone acrylic copolymer obtained by reacting an oxidative curing acrylic copolymer (a) obtained by graft polymerizing monomers illustrated in following (a-1), (a-2), and (a-3) into an alkyd resin (c) having an oxidative polymerizable group, and a silicone (b) having at least one of a hydroxyl group and an alkoxy group,

in a raw material, 8 to 40% by mass of the alkyd resin (c), 10 to 30% by mass of the styrenes (a-1), and 5 to 15% by mass of the silicone (b) are contained in a total amount of the alkyd resin (c), the styrenes (a-1), the (meth)acrylic acid ester (a-2), the polymerizable unsaturated monomer (a-3), and the silicone (b).

(a-1) styrenes;

(a-2) a (meth)acrylic acid ester; and

(a-3) a polymerizable unsaturated monomer having at least one of functional group selected from the group consisting of a hydroxyl group, a carboxyl group, a glycidyl group, and an isocyanate group

2. The oxidative curing alkyd-modified silicone acrylic copolymer according to claim 1, wherein the styrenes (a-1), the (meth)acrylic acid ester (a-2), and the polymerizable unsaturated monomer (a-3) are respectively contained in following proportions in a

total amount of the styrenes (a-1), the (meth)acrylic acid ester (a-2), and the polymerizable unsaturated monomer (a-3).

(a-1) the styrenes: 13 to 40% by mass

(a-2) the (meth)acrylic acid ester: 53 to 86% by mass; and

(a-3) the polymerizable unsaturated monomer: 1 to 7% by mass

3. The oxidative curing alkyd-modified silicone acrylic copolymer according to claim 1 or 2, wherein the styrenes (a-1), the (meth)acrylic acid ester (a-2), and the polymerizable unsaturated monomer (a-3) are contained in a proportion of 45 to 87% by mass in total in the oxidative curing alkyd-modified silicone acrylic copolymer.

4. The oxidative curing alkyd-modified silicone acrylic copolymer according to any one of claims 1 to 3, having a solid iodine value of 5 to 50.

5. The oxidative curing alkyd-modified silicone acrylic copolymer according to any one of claims 1 to 4, having a weight average molecular weight of 10,000 to 150,000.

6. The oxidative curing alkyd-modified silicone

acrylic copolymer according to any one of claims 1 to 5, wherein the silicone (b) further has a phenyl group.

7. A method for producing an oxidative curing alkyd-modified silicone acrylic copolymer, the method comprising the steps of:

obtaining an oxidative curing acrylic copolymer (a) by graft polymerizing monomers illustrated in following (a-1), (a-2), and (a-3) into an alkyd resin (c) having an oxidative polymerizable group; and

reacting the obtained oxidative curing acrylic copolymer (a) and a silicone (b) having at least one of a hydroxyl group and an alkoxy group,

8 to 40% by mass of the alkyd resin (c), 10 to 30% by mass of the styrenes (a-1), and 5 to 15% by mass of the silicone (b) are used in a total amount of the alkyd resin (c), the styrenes (a-1), the (meth)acrylic acid ester (a-2), the polymerizable unsaturated monomer (a-3), and the silicone (b).

(a-1) styrenes;

(a-2) a (meth)acrylic acid ester; and

(a-3) a polymerizable unsaturated monomer having at least one of functional group selected from the group consisting of a hydroxyl group, a carboxyl group, a glycidyl group, and an isocyanate group

ABSTRACT

An oxidative curing alkyd-modified silicone acrylic copolymer of the present invention is obtained by reacting an oxidative curing acrylic copolymer (a) and a silicone (b) having at least one of a hydroxyl group and an alkoxy group. The oxidative curing acrylic copolymer (a) is a copolymer obtained by graft polymerizing monomers indicated in (a-1) styrenes, (a-2) a (meth)acrylic acid ester, and (a-3) a predetermined polymerizable unsaturated monomer into an alkyd resin (c) having an oxidative polymerizable group.