

COATING RESIN COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a resin composition, particularly a coating resin composition.

BACKGROUND OF THE INVENTION

Films for protecting, e.g., outside walls of buildings are required to have excellent durability and excellent weather resistance. As coating resins for forming such films, resin compositions containing a large amount of a silicone resin are known. For example, a coating resin comprising an acrylic or polyester resin that an alcoholic hydroxyl group-containing polyorganosiloxane resin is incorporated therein is disclosed in JP-A-2-64181. (The term "JP-A" as used herein means an "unexamined published Japanese patent application.")

In addition to durability and weather resistance, the films described above are required to have anti-pollution properties as a function of maintaining the appearance thereof. Since it is generally thought that the anti-pollution properties of a film are closely related with the stickiness and electrostatic properties of the film, improvements of the anti-pollution properties of films are attempted in view of these factors. For example, a constitution in which the stickiness of a film is reduced by heightening the hardness thereof to thereby physically



inhibit contaminants from adhering to the film has been proposed. Other proposed constitutions include one in which a hydrophilic property-providing agent such as a sulfonium salt of an alkali metal is added to a paint to form a film having reduced electrostatic properties and thereby to inhibit contaminants from electrostatically adhering to the film.

However, improvements in anti-pollution properties of a film with respect to stickiness or electrostatic properties often result in impairments in general film performances including weather resistance, adhesive properties, and flexibility. For example, an increase in film hardness results in impaired flexibility of the film, while a reduction in the electrostatic properties of a film by means of a hydrophilic property-providing agent results in impairments in the weather resistance and adhesive properties of the film due to the hydrophilic property-providing agent added to the paint. It is thus difficult to improve the anti-pollution properties of a film while maintaining general properties required of the film.

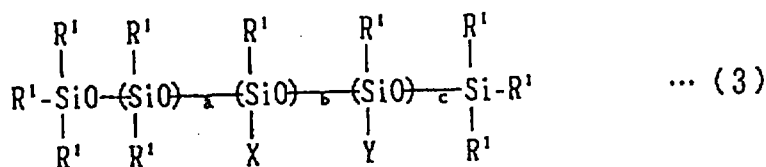
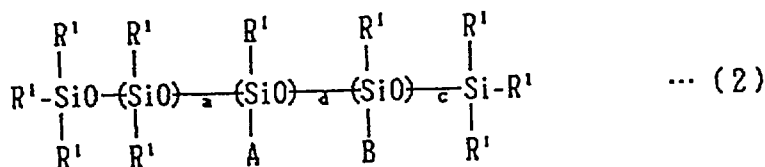
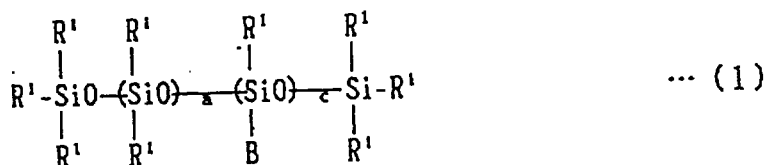
Although it has been proposed to improve the anti-pollution properties of a film by regulating the surface roughness of the film, this technique is effective only in making the contamination of the film less noticeable and, hence, cannot be a means for essentially improving anti-pollution properties.

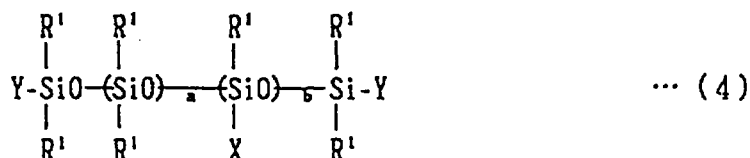


SUMMARY OF THE INVENTION

An object of the present invention is to improve the anti-pollution properties of a film while maintaining generally required-film properties including weather resistance.

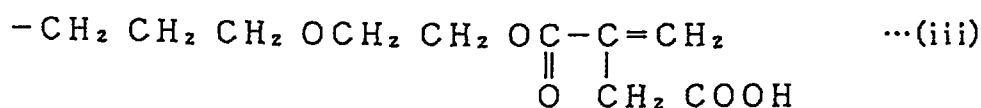
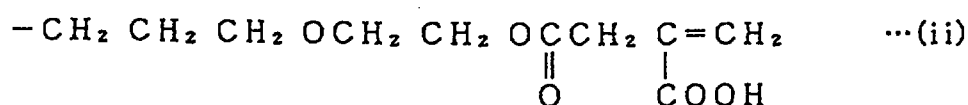
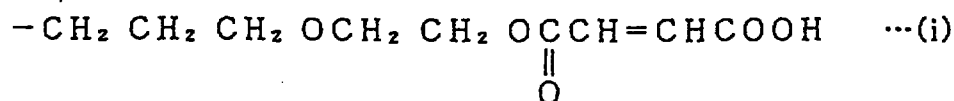
The coating resin composition of the present invention comprises a silicone compound (A), a hydroxyl group-containing resin (B), and a crosslinking agent (C) having a functional group reactive with a hydroxyl group. The silicone compound is at least one compound selected from the group consisting of the silicone compounds represented by average composition formulae (1), (2), (3), and (4). At least part of the functional groups contained in at least one of the silicone compound and the hydroxyl group-containing resin is present in the form of a salt.





In the above formulae,

A is at least one organic residue selected from the group consisting of the organic residues represented by chemical formulae (i), (ii), and (iii):



B is $-CH_2CH_2CH_2OCH_2CH_2OH$,

X is a 3-acryloxypropyl group or a 3-methacryloxypropyl group,

Y is a monovalent substituent containing at least one group selected from the group consisting of $-COOH$, $-SO_3H$, and $-NR^2_2$ (wherein R^2 is an organic residue),

R^1 is an aryl group, an aralkyl group, or an alkyl group having 1 to 6 carbon atoms, and

a, b, c, and d each are the following repeating-unit numbers.

$$1 \leq a \leq 20$$



$$0.5 \leq b \leq 3$$

$$1 \leq c \leq 10$$

$$0 < d \leq 6$$

In this coating resin composition, a part or all of the silicone compound may have been bonded to a part of the hydroxyl group-containing resin to form a silicone-modified resin.

The hydroxyl group-containing resin has a hydroxyl value of, for example, from 20 to 300 (especially preferably from 40 to 120).

The mixing ratio ((A):(B)) of the silicone compound (A) to the hydroxylated resin (B) is, for example, from 3:97 to 70:30 (especially preferably from 5:95 to 40:60).

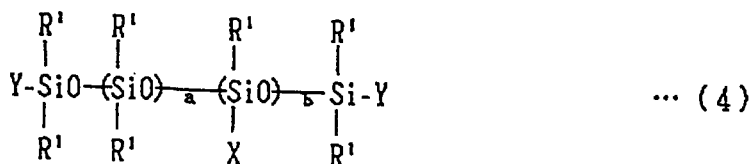
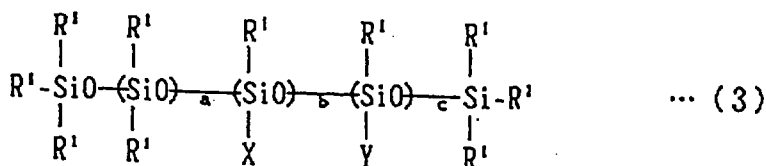
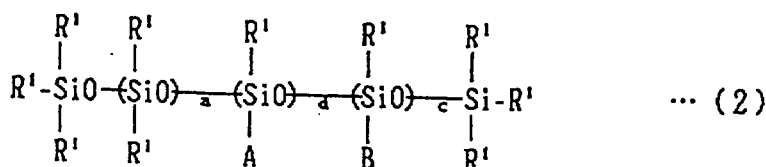
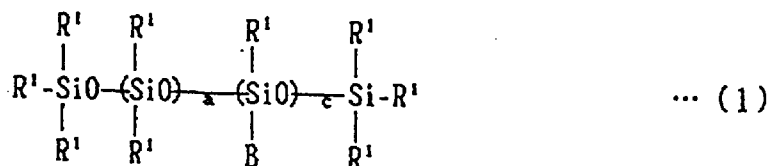
DETAILED DESCRIPTION OF THE INVENTION

Silicone Compound (A)

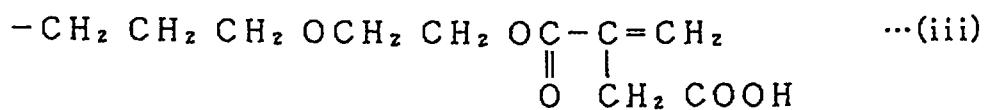
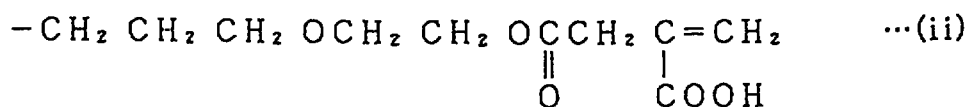
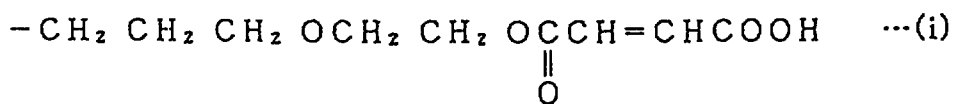
The silicone compounds that can be used in the present invention are represented by average composition formulae (1), (2), (3), and (4). In the present invention, these silicone compounds may be used either alone or in combination of two or more thereof.

This Sheet Has Been Replaced

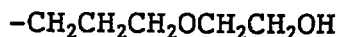




In these silicone compounds, A is at least one organic residue selected from the group consisting of the organic residues represented by formulae (i), (ii), and (iii).



B is the group represented by chemical formula.



X is a 3-acryloxypropyl group or a 3-methacryloxypropyl group. Y is a monovalent substituent containing at least one group selected from the group consisting of $-\text{COOH}$, $-\text{SO}_3\text{H}$, and $-\text{NR}^2$. This group represented by Y may be linear or branched. R^2 is preferably an organic residue containing hydrogen. This organic residue is not particularly limited, and examples thereof include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, and t-butyl. Two or more kinds of X and two or more kinds of Y may be contained in one silicone compound (that is, two or more different groups represented by X and two or more different groups represented by Y may be present).

In the silicone compounds described above, R^1 is an aryl group (e.g., phenyl or naphthyl), an aralkyl group (e.g., nonylphenyl), or an alkyl group having 1 to 6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, or hexyl). From an industrial standpoint, R^1 is preferably methyl or phenyl. Two or more kinds of R^1 may be contained in one silicone compound (that is, two or more different groups represented by R^1 may be present).

In the average composition formulae (1) to (4) showing the silicone compounds, a, b, c, and d each are the following repeating-unit numbers.



$$1 \leq a \leq 20$$

$$0.5 \leq b \leq 3$$

$$1 \leq c \leq 10$$

$$0 < d \leq 6$$

Preferably, a, b, c, and d each are the following numbers.

$$2 \leq a \leq 15$$

$$0.7 \leq b \leq 1.5$$

$$2 \leq c \leq 7$$

$$0.5 < d \leq 3$$

If a is smaller than 1, the weather resistance of a film cannot be improved by the silicone compounds. If a exceeds 20, silicone compounds have impaired reactivity and compatibility with an α, β -ethylenically-unsaturated monomer. If b is smaller than 0.5, the copolymerization proportion of silicone compounds to a α, β -ethylenically-unsaturated monomer is reduced, and this may result in an increased content of residual unreacted silicone compounds and impaired copolymer resin properties. If b exceeds 3 or if d exceeds 6, gelation occurs during polymerization of silicone compounds with an α, β -ethylenically-unsaturated monomer, so that satisfactory film-forming properties are not exhibited. If c is smaller than 1, it is difficult to impart sufficient hydrophilic property to the film of the present invention. If c exceeds 10, the compounds have an increased viscosity, and the reactivity and compatibility thereof with an α, β -ethylenically-unsaturated monomer are reduced.



In each of the silicone compounds respectively represented by the average composition formulae (1), (2), (3), and (4) described above, the repeating units may have been arranged block-wise, randomly, or alternately.

The silicone compound (A) used in the present invention can be obtained as follows.

(I) Silicone compound represented by average composition formula (1)

This silicone compound is commercially available. For example, silicone compound "KR-9206" (manufactured by Shin-Etsu Chemical Industry Co., Ltd., Japan) is utilizable as the silicone compound represented by average composition formula (1).

(II) Silicone compound represented by average composition formula (2)

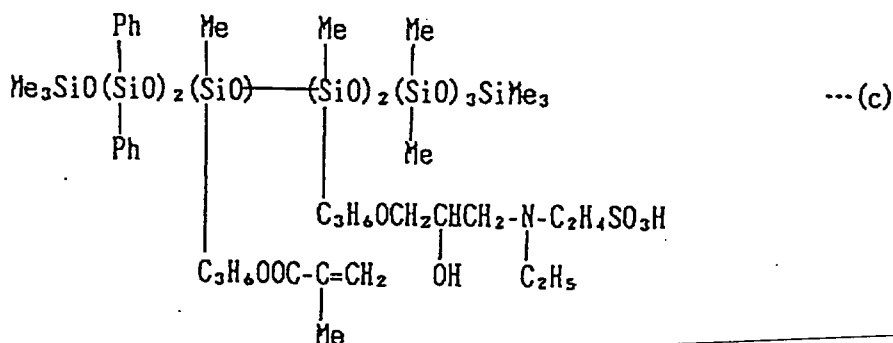
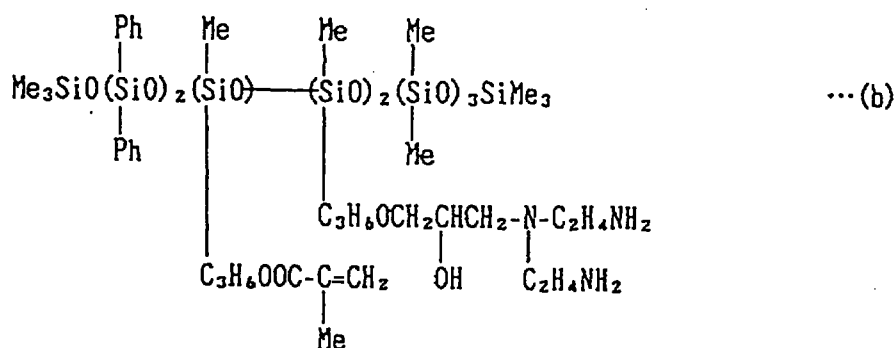
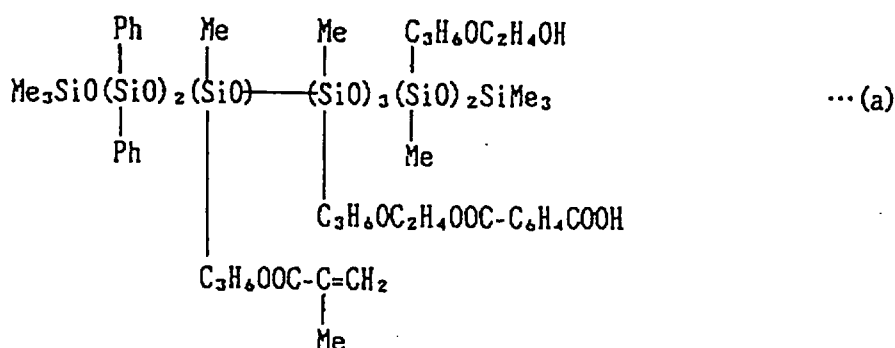
This silicone compound can be synthesized by reacting the silicone compound represented by average composition formula (1) with maleic anhydride or itaconic anhydride. Specifically, the silicone compound represented by average composition formula (1) is brought into contact with maleic anhydride, upon which the terminal OH group of B in the silicone compound undergoes esterification reaction with the maleic anhydride to obtain a silicone compound having A represented by formula (i) described above. When the silicone compound represented by average composition formula (1) is brought into contact with itaconic anhydride,



esterification reaction occurs likewise to obtain a silicone compound having A represented by formulae (ii) and (iii).

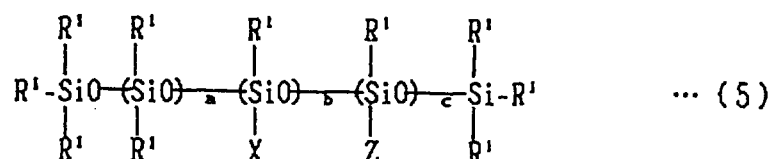
(III) Silicone compound represented by average composition formula (3)

Examples of this silicone compound include the compounds represented by the following structural formulae. In the structural formulae given herein, Me and Ph represent a methyl group and a phenyl group, respectively.



This kind of silicone compounds can be synthesized through the following route.

First, a silicone compound represented by average composition formula (5) is synthesized.



In the above formula (5),

X is a 3-acryloxypropyl group or a 3-methacryloxypropyl group,

Z is at least one group selected from the group consisting of 3-glycidoxypropyl, 2-(3',4'-epoxycyclohexyl)ethyl, 3-hydroxypropyl, 3-(2'-hydroxyethoxy)propyl, and 3-(4'-(3',3'-hydroxymethyl)butoxy)propyl,

R¹ is an aryl group, an aralkyl group, or an alkyl group having 1 to 6 carbon atoms, and

a, b, and c each are the following repeating-unit numbers.

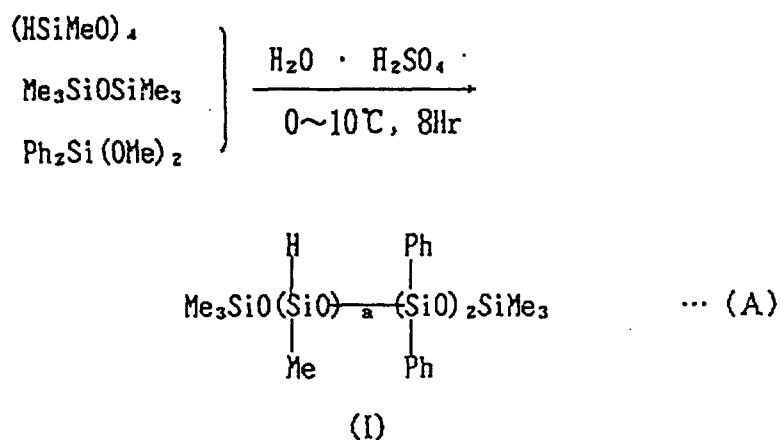
$$1 \leq a \leq 20$$

$$0.5 \leq b \leq 3$$

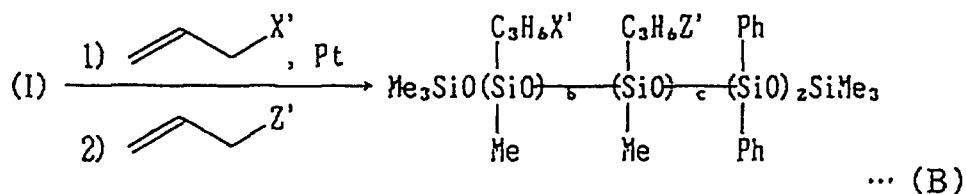
$$1 \leq c \leq 10$$

This silicone compound can be synthesized by the hydrosilylation reaction of a phenylmethylhydrogenpolysiloxane with an alkene having an organic functional group. This phenylmethylhydrogenpolysiloxane can be synthesized, for example, by the following reaction (A).

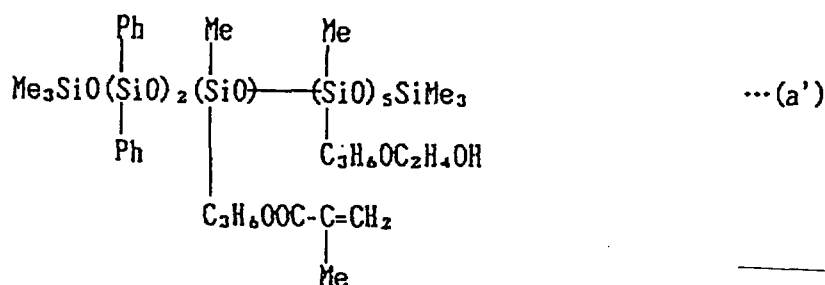




From the phenylmethylhydrogenpolysiloxane, the desired silicone compound can be synthesized, for example, by the following reaction (B).



In the case of synthesizing compounds (a), (b), and (c) enumerated above as examples of the silicone compound represented by average composition formula (3), the following silicone compounds (a') and (b') are synthesized according to the method described above.



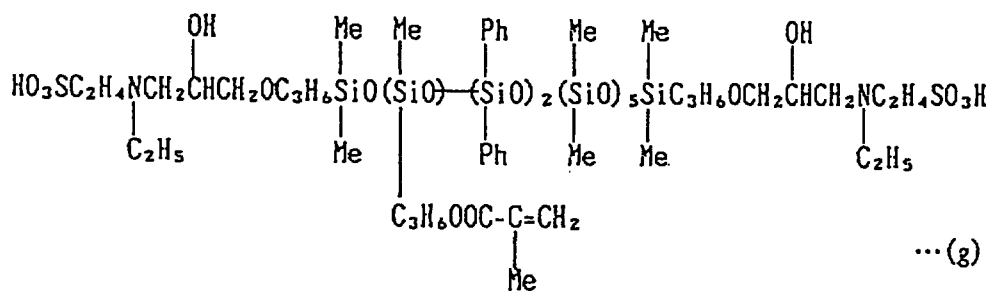
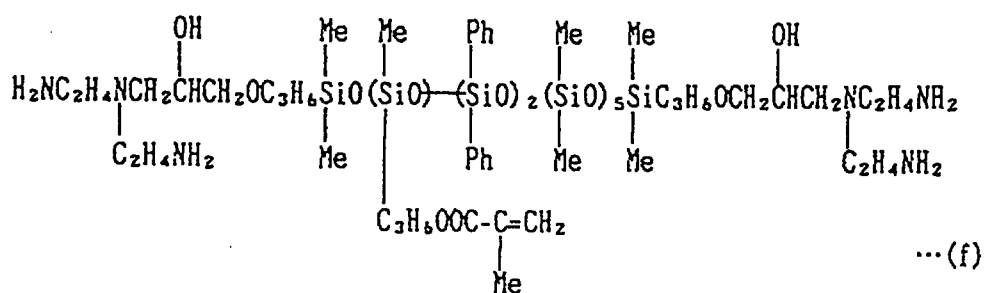
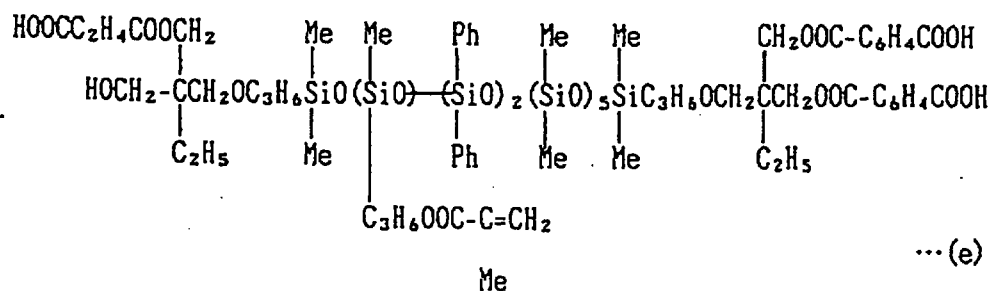
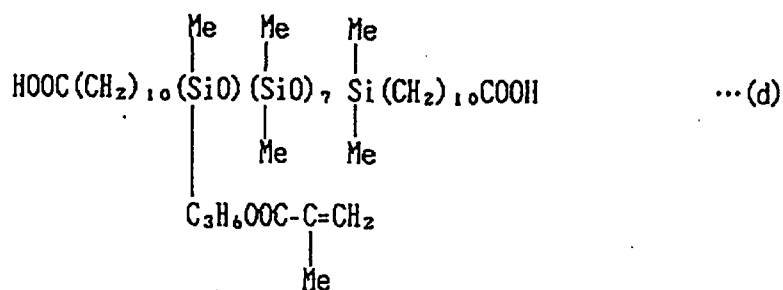
(a') $\xrightarrow{\text{acid anhydride (hexahydrophthalic anhydride)}} \text{(a)}$

(b') $\xrightarrow{\text{amine compound } \text{HN}(\text{CH}_2\text{CH}_2\text{N}=\underset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{CH}_2\text{CH}(\text{CH}_3)_2)_2} \text{---CH}_3\text{C}(\overset{\text{O}}{\parallel})\text{CH}_2\text{CH}(\text{CH}_3)_2} \text{(b)}$

(b') $\xrightarrow{\text{sulfonic acid compound } \text{HN}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{SO}_3\text{H}} \text{(c)}$

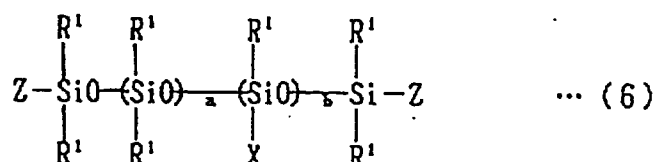
Examples of this silicone compound include the following compounds.





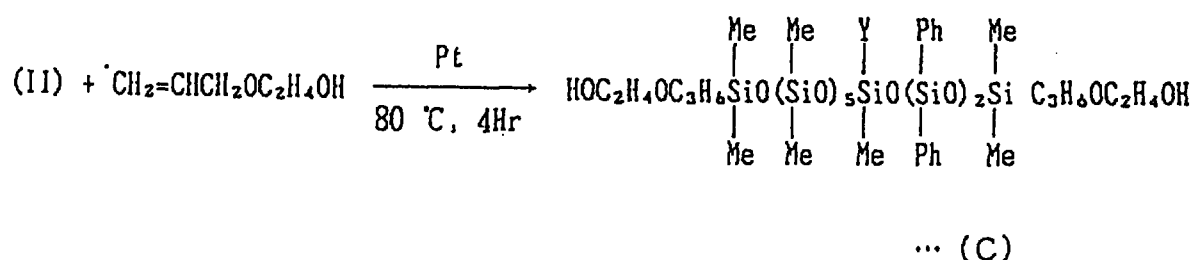
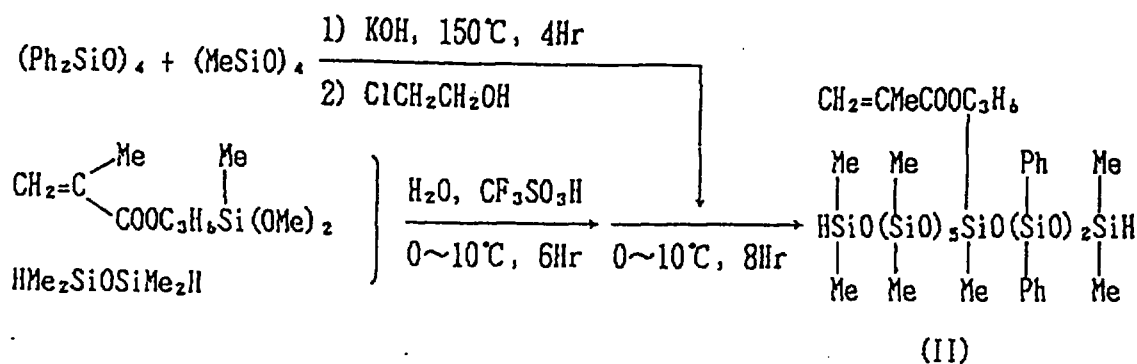
This silicone compound can be synthesized through the following route.

First, a silicone compound represented by average composition formula (6) is synthesized. In formula (6), X, Z, R¹, a, and b have the same meanings as in average composition formula (5).

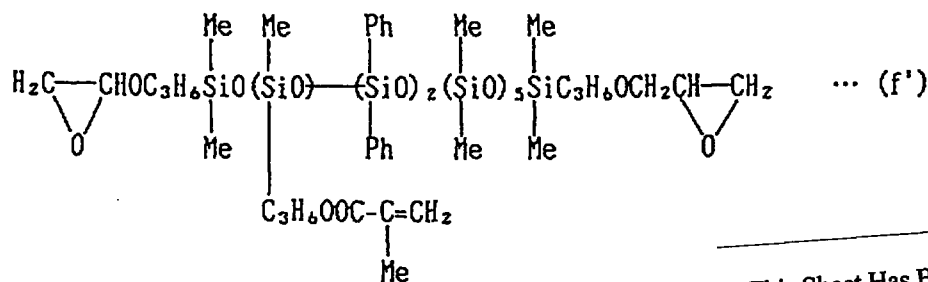
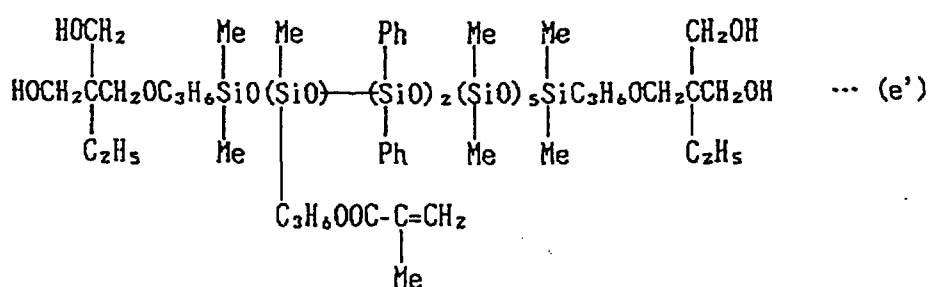


This silicone compound can be synthesized, for example, from a reaction product obtained by reacting tetramethyldisiloxane with 3-methacryloxypropylmethyl-dimethoxysilane and water in the presence of an acid catalyst and from a reaction product obtained by equilibrating octamethylcyclotetrasiloxane and octaphenylcyclotetrasiloxane with an alkali, by subjecting the two reaction products to an equilibrating reaction with trifluoromethanesulfonic acid. This synthesis route is shown below as (C).

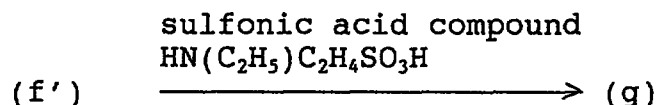
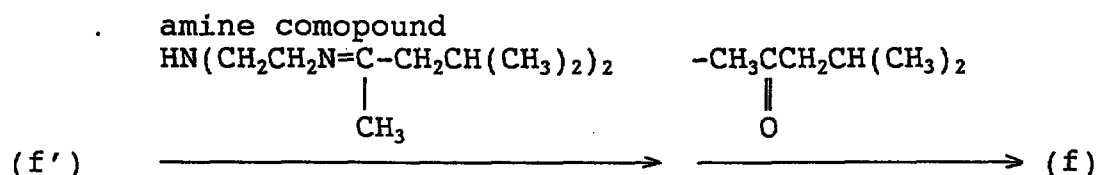
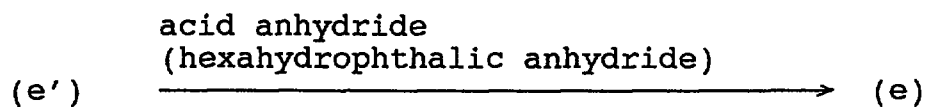




In the case of synthesizing compounds (e), (f), and (g) enumerated above as examples of the silicone compound represented by average composition formula (4), the following silicone compounds (e') and (f') are synthesized according to the method described above.



Modifying these compounds (e') and (f') with an acid anhydride, an amine compound, or a sulfonic acid compound gives the desired silicone compounds (e), (f), and (g). Specifically, these reactions are as follows.



Compound (11) given above as an example of the silicone compound represented by average composition formula (4) can be synthesized by adding the following allyl compound to the above-specified compound (II) in the synthesis route (C) of the silicone compound represented by average composition formula (6).



The above-described silicone compounds used in the present invention have a number-average molecular weight of from 200 to 100,000, preferably from 500 to 20,000. If the



number-average molecular weight thereof is lower than 200, it is difficult to form a film having sufficient mechanical strength. On the other hand, number-average molecular weights thereof exceeding 100,000 result in impaired compatibility with the hydroxyl group-containing resin and the crosslinking agent, making it difficult to obtain a sufficiently cured film. Number-average molecular weight herein is determined by Gel-Permeation Chromatography (GPC).

Hydroxyl Group-containing Resin (B)

The hydroxyl group-containing resin used in the present invention is not particularly limited, and resins of all kinds may be used as long as they contain a hydroxyl group. Representative examples of the hydroxyl group-containing resin include acrylic resins, alkyd resins, polyester resins, epoxy resins, aminoplast resins, acryl-modified alkyd resins, acryl-modified polyester resins, and polycarbonate resins.

Especially preferred of the hydroxyl group-containing resins used in the present invention are those having a hydroxyl value of from 20 to 300, preferably from 30 to 100. If a hydroxyl group-containing resin having a hydroxyl value of lower than 20 is used, the reaction of this resin with the crosslinking agent is insufficient, resulting in impaired mechanical physical property. If a hydroxyl group-containing resin having a hydroxyl value of higher than 300 is used, this resin has poor compatibility with the crosslinking



agent, so that a sufficiently cured film is not obtained.

Crosslinking Agent (C)

The crosslinking agent in the present invention is used for forming crosslinks between molecules of the silicone compound, between molecules of the hydroxyl group-containing resin, or between the silicone compound and the hydroxyl group-containing resin.

In the present invention, any compound having in the molecule thereof a functional group reactive with a hydroxyl group can be used as the crosslinking agent without particular limitations. Examples of the crosslinking agent include polyisocyanate compounds, melamine-formaldehyde resins, and dibasic acid anhydrides. When this kind of crosslinking agents are used, the functional groups contained therein react with hydroxyl groups contained in both the silicone compound and the hydroxyl group-containing resin at room temperature or an elevated temperature to three-dimensionally crosslink the silicone compound and the hydroxyl group-containing resin, thereby giving a film having improved mechanical strength.

Use of a crosslinking agent having a hydrophilic segment is effective in giving a film having further improved anti-pollution properties. Examples of the crosslinking agent having a hydrophilic segment include poly(ethylene glycol)-modified isocyanate "N2-753" (manufactured by Dai-Nippon Ink & Chemicals, Inc., Japan).



Resin Composition

The coating resin composition of the present invention comprises the silicone compound, hydroxyl group-containing resin, and crosslinking agent described above. A part or all of the functional groups possessed by the silicone compound and hydroxyl group-containing resin described above should be in the form of a salt. That is, a part or all of the acid functional groups or basic functional groups contained in both the silicone compound and the hydroxyl group-containing resin should be in the form of a salt. A representative technique for forming a salt is to neutralize the silicone compound and the hydroxyl group-containing resin with an acid or an alkali. In the case of the hydroxyl group-containing resin, a salt structure may be formed therein during the synthesis thereof by, for example, using a comonomer having a salt structure, such as sodium styrenesulfonate.

In the resin composition of the present invention, the mixing ratio ((A):(B)) of the silicone compound (A) to the hydroxylated resin (B) is regulated to from 3:97 to 70:30, more preferably from 5:95 to 40:60. If the proportion of the silicone compound is below 3, the properties of the silicone compound are not sufficiently exhibited, resulting, for example, in impaired weather resistance of the film. On the other hand, if the proportion of the silicone compound exceeds 70, compatibility between the silicone compound and



the hydroxyl group-containing resin is impaired, resulting in a film having reduced hardness and impaired anti-pollution properties.

The crosslinking agent is added in an amount necessary for the progress of the crosslinking reaction. Although this addition amount is not particularly limited, it is usually from 10 to 30% by weight based on the amount of the mixture of the silicone compound and the hydroxyl group-containing resin.

In the resin composition of the present invention, a part or all of the silicone compound may have been bonded to a part of the hydroxyl group-containing resin to form a silicone-modified resin. This composition is preferred in that it gives a film having further heightened weather resistance. Methods for bonding the silicone compound to the hydroxyl group-containing resin are not particularly limited. Examples thereof include a method in which the silicone compound is added during the synthesis of the hydroxyl group-containing resin to modify the hydroxyl group-containing resin with the silicone compound. Another usable method comprises adding a polyurethane resin, a melamine-formaldehyde resin, a dibasic acid anhydride, or the like to thereby bond the silicone compound to the hydroxyl group-containing resin.

Utilization of coating resin composition

The coating resin composition of the present



invention is used as a paint after being mixed with, e.g., a coloring pigment, an extender pigment, a necessary solvent, and general additives. This paint can be utilized, e.g., as a paint for outside building walls.

The film formed from the paint containing the resin composition of the present invention has a moderately hydrophilic surface due to the salt structure formed in at least part of the silicone compound and hydroxyl group-containing resin. The degree of this hydrophilic property is usually 65° or lower in terms of contact angle with water. Since contaminants adherent to this film can hence be easily removed with water, this film has excellent anti-pollution properties. Moreover, this film also has excellent properties in general film properties including weather resistance, durability, and flexibility because of the silicone compound contained in the resin components.

The present invention will be explained below in more detail by reference to the following Examples, but the invention should not be construed as being limited thereto.

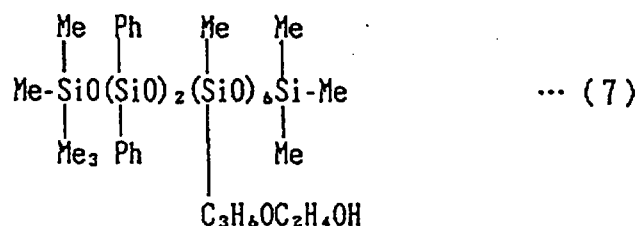
Hereinafter, all "parts" are by weight.

PRODUCTION EXAMPLE 1 (Synthesis of Silicone Compound)

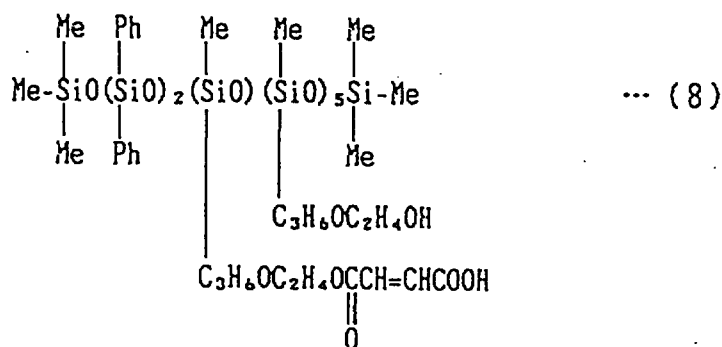
A mixture of 40 parts of the silicone compound represented by the following average composition formula (7), 44 parts of xylol, 4 parts of maleic anhydride, and 0.5 parts of dibutyltin oxide was reacted at 100°C for 1 hour. This reaction was traced by infrared absorption spectrum (IR), by



which completion of the reaction was ascertained.

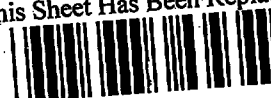


Thus, a solution of the silicone compound represented by the following average composition formula (8) was obtained. This silicone compound corresponds to the silicone compound represented by the average composition formula (2) described hereinabove.



PRODUCTION EXAMPLE 2 (Synthesis of Silicone-Modified Acrylic Resin Solution)

To a reaction mixture containing 40 parts of the silicone compound solution obtained in Production Example 1 and 70 parts of xylol and maintained at 110°C was added dropwise over a period of 3 hours a solution containing 10 parts of methacrylic acid, 20 parts of 2-hydroxyethyl



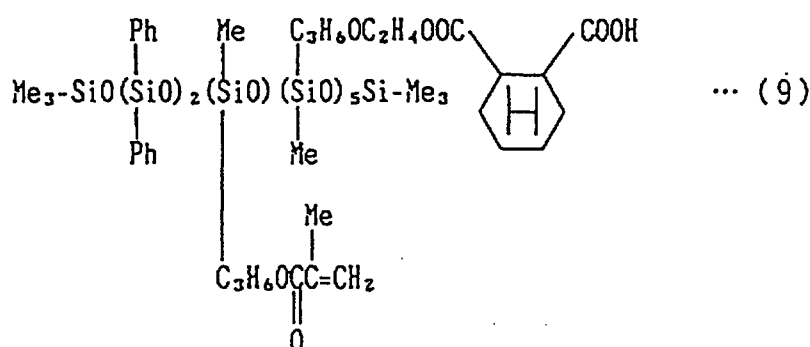
methacrylate, 25 parts of 2-ethylhexyl methacrylate, 25 parts of t-butyl methacrylate, and 2 parts of t-butyl peroxy-2-ethylhexanoate. After this mixture was aged for 1 hour, 0.5 parts of t-butyl peroxy-2-ethylhexanoate and 30 parts of xylol were added thereto dropwise over a period of 30 minutes, and the resulting mixture was aged for 2 hours. As a result, a solution of a silicone-modified acrylic resin was obtained. The silicone-modified acrylic resin contained in this solution corresponds to the resin formed by bonding a silicone compound to a hydroxyl group-containing resin. In this silicone-modified acrylic resin, the acrylic resin moiety had a hydroxyl value of 86.

PRODUCTION EXAMPLE 3 (Synthesis of Silicone-Modified Acrylic Resin Solution)

To a reaction mixture containing 20 parts of the silicone compound represented by the following average composition formula (9) and 70 parts of xylol and maintained at 110°C was added dropwise over a period of 3 hours a solution containing 10 parts of methacrylic acid, 20 parts of 2-hydroxyethyl methacrylate, 25 parts of 2-ethylhexyl methacrylate, 25 parts of t-butyl methacrylate, and 2 parts of t-butyl peroxy-2-ethylhexanoate. After this mixture was aged for 1 hour, 0.5 parts of t-butyl peroxy-2-ethylhexanoate and 30 parts of xylol were added thereto dropwise over a period of 30 minutes, and the resulting mixture was aged for 2 hours. As a result, a solution of a silicone-modified



acrylic resin was obtained. The silicone-modified acrylic resin contained in this solution corresponds to the resin formed by bonding a silicone compound to a hydroxyl group-containing resin. In this silicone-modified acrylic resin, the acrylic resin moiety had a hydroxyl value of 86.

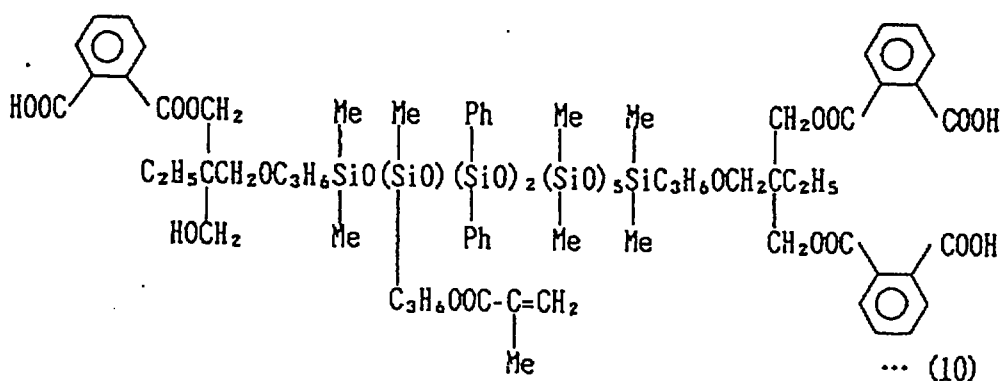


PRODUCTION EXAMPLE 4 (Synthesis of Silicone-Modified Acrylic Resin Solution)

To a reaction mixture containing 20 parts of the silicone compound represented by the following average composition formula (10) and 70 parts of xylol and maintained at 110°C was added dropwise over a period of 3 hours a solution containing 10 parts of methacrylic acid, 20 parts of 2-hydroxyethyl methacrylate, 25 parts of 2-ethylhexyl methacrylate, 25 parts of t-butyl methacrylate, and 2 parts of t-butyl peroxy-2-ethylhexanoate. After this mixture was aged for 1 hour, 0.5 parts of t-butyl peroxy-2-ethylhexanoate and 30 parts of xylol were added thereto dropwise over a period of 30 minutes, and the resulting mixture was aged for



2 hours. As a result, a solution of a silicone-modified acrylic resin was obtained. The silicone-modified acrylic resin contained in this solution corresponds to the resin formed by bonding a silicone compound to a hydroxyl group-containing resin. In this silicone-modified acrylic resin, the acrylic resin moiety had a hydroxyl value of 86.



PRODUCTION EXAMPLE 5 (Synthesis of Silicone-Modified Acrylic Resin Solution)

To a reaction mixture containing 38 parts of the silicone compound solution obtained in Production Example 1, 1 part of the silicone compound represented by average composition formula (9) used in Production Example 3 and 71 parts of xylol and maintained at 110°C was added dropwise over a period of 3 hours a solution containing 10 parts of methacrylic acid, 20 parts of 2-hydroxyethyl methacrylate, 25 parts of 2-ethylhexyl methacrylate, 25 parts of t-butyl methacrylate, and 2 parts of t-butyl peroxy-2-ethylhexanoate. After this mixture was aged for 1 hour, 0.5 parts of t-butyl



peroxy-2-ethylhexanoate and 30 parts of xylol were added thereto dropwise over a period of 30 minutes, and the resulting mixture was aged for 2 hours. As a result, a solution of a silicone-modified acrylic resin was obtained. The silicone-modified acrylic resin contained in this solution corresponds to the resin formed by bonding a silicone compound to a hydroxyl group-containing resin. In this silicone-modified acrylic resin, the acrylic resin moiety had a hydroxyl value of 86.

PRODUCTION EXAMPLE 6 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Sodium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 2 was mixed with 11 parts of a 40 wt% ethanolic solution of sodium hydroxide. The solvent was removed from this solution by distillation under the reduced pressure, and the residue was dissolved in a mixture of 50 parts of xylol and 50 parts of methyl isobutyl ketone. Thus, a solution of a silicone-modified acrylic resin containing a sodium salt was obtained.

PRODUCTION EXAMPLE 7 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Sodium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 3 was treated in the same manner as in Production Example 6 to obtain a solution of a silicone-modified acrylic resin containing a sodium salt.



PRODUCTION EXAMPLE 8 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Sodium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 4 was treated in the same manner as in Production Example 6 to obtain a solution of a silicone-modified acrylic resin containing a sodium salt.

PRODUCTION EXAMPLE 9 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Sodium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 5 was treated in the same manner as in Production Example 6 to obtain a solution of a silicone-modified acrylic resin containing a sodium salt.

PRODUCTION EXAMPLE 10 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Potassium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 2 was mixed with 26 parts of a 25 wt%-ethanolic solution of potassium hydroxide. The solvent was removed from this solution by distillation under the reduced pressure, and the residue was dissolved in a mixture of 50 parts of xylol and 50 parts of methyl isobutyl ketone. Thus, a solution of a silicone-modified acrylic resin containing a potassium salt was obtained.



PRODUCTION EXAMPLE 11 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Potassium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 3 was treated in the same manner as in Production Example 10 to obtain a solution of a silicone-modified acrylic resin containing a potassium salt.

PRODUCTION EXAMPLE 12 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Potassium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 4 was treated in the same manner as in Production Example 10 to obtain a solution of a silicone-modified acrylic resin containing a potassium salt.

PRODUCTION EXAMPLE 13 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Potassium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 5 was treated in the same manner as in Production Example 10 to obtain a solution of a silicone-modified acrylic resin containing a potassium salt.

PRODUCTION EXAMPLE 14 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Lithium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 2 was mixed with 11 parts of a 25 wt%-ethanolic solution of lithium hydroxide.



The solvent was removed from this solution by distillation under the reduced pressure, and the residue was dissolved in a mixture of 50 parts of xylol and 50 parts of methyl isobutyl ketone. Thus, a solution of a silicone-modified acrylic resin containing a lithium salt was obtained.

PRODUCTION EXAMPLE 15 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Lithium Salt)

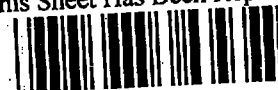
200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 3 was treated in the same manner as in Production Example 14 to obtain a solution of a silicone-modified acrylic resin containing a lithium salt.

PRODUCTION EXAMPLE 16 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Lithium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 4 was treated in the same manner as in Production Example 14 to obtain a solution of a silicone-modified acrylic resin containing a lithium salt.

PRODUCTION EXAMPLE 17 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Lithium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 5 was treated in the same manner as in Production Example 14 to obtain a solution of a silicone-modified acrylic resin containing a lithium salt.



PRODUCTION EXAMPLE 18 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Triethylamine Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 2 was mixed with 47 parts of a 25 wt%-ethanolic solution of triethylamine. The solvent was removed from this solution by distillation under the reduced pressure, and the residue was dissolved in a mixture of 50 parts of xylol and 50 parts of methyl isobutyl ketone. Thus, a solution of a silicone-modified acrylic resin containing a triethylamine salt was obtained.

PRODUCTION EXAMPLE 19 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Triethylamine Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 3 was treated in the same manner as in Production Example 18 to obtain a solution of a silicone-modified acrylic resin containing a triethylamine salt.

PRODUCTION EXAMPLE 20 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Triethylamine Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 4 was treated in the same manner as in Production Example 18 to obtain a solution of a silicone-modified acrylic resin containing a triethylamine salt.



PRODUCTION EXAMPLE 21 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Triethylamine Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 5 was treated in the same manner as in Production Example 18 to obtain a solution of a silicone-modified acrylic resin containing a triethylamine salt.

PRODUCTION EXAMPLE 22 (Synthesis of Acrylic Resin Solution)

To a reaction mixture containing 70 parts of xylol and maintained at 110°C was added dropwise over a period of 3 hours a solution containing 10 parts of methacrylic acid, 20 parts of 2-hydroxyethyl methacrylate, 25 parts of 2-ethylhexyl methacrylate, 25 parts of t-butyl methacrylate, and 2 parts of t-butyl peroxy-2-ethylhexanoate. After this mixture was aged for 1 hour, 0.5 parts of t-butyl peroxy-2-ethylhexanoate and 30 parts of xylol were added thereto dropwise over a period of 30 minutes, and the resulting mixture was aged for 2 hours. Thereafter, 20 parts of the silicone compound represented by the average composition formula (7) described hereinabove was added thereto to obtain an acrylic resin solution.

PRODUCTION EXAMPLE 23 (Synthesis of Acrylic Resin Solution Containing Sodium Salt)

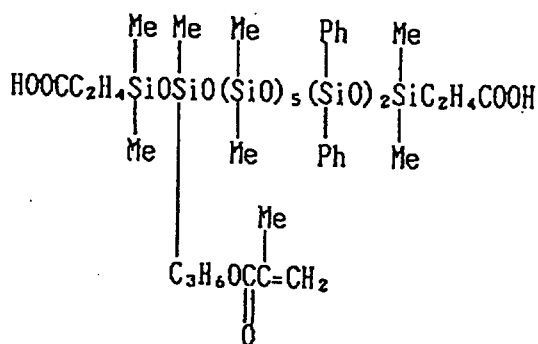
200 Parts of the acrylic resin solution synthesized in Production Example 22 was treated in the same manner as in Production Example 6 to obtain a solution of an acrylic resin



containing a sodium salt.

PRODUCTION EXAMPLE 24 (Synthesis of Silicone-Modified Acrylic Resin Solution)

To a reaction mixture containing 20 parts of the silicone compound represented by the following average composition formula and 70 parts of xylol and maintained at 110°C was added dropwise over a period of 3 hours a solution containing 8 parts of methacrylic acid, 20 parts of 2-hydroxyethyl methacrylate, 27 parts of 2-ethylhexyl methacrylate, 25 parts of t-butyl methacrylate, and 2 parts of t-butyl peroxy-2-ethylhexanoate. After this mixture was aged for 1 hour, 0.5 parts of t-butyl peroxy-2-ethylhexanoate and 30 parts of xylol were added thereto dropwise over a period of 30 minutes, and the resulting mixture was aged for 2 hours. As a result, a solution of a silicone-modified acrylic resin was obtained. The silicone-modified acrylic resin contained in this solution corresponds to the resin formed by bonding a silicone compound to a hydroxyl group-containing resin.



----- (11)



PRODUCTION EXAMPLE 25 (Synthesis of Silicone-Modified Acrylic Resin Solution Containing Sodium Salt)

200 Parts of the silicone-modified acrylic resin solution synthesized in Production Example 24 was treated in the same manner as in Production Example 6 to obtain a solution of a silicone-modified acrylic resin containing a sodium salt.

PRODUCTION EXAMPLE 26 (Synthesis of Mixed Solution of Hydroxyl Group-Containing Acrylic Resin and Silicone-Modified Acrylic Resin)

To a reaction mixture containing 70 parts of xylol and maintained at 110°C was added dropwise over a period of 3 hours a solution containing 10 parts of methacrylic acid, 20 parts of 2-hydroxyethyl methacrylate, 25 parts of 2-ethylhexyl methacrylate, 25 parts of t-butyl methacrylate, and 2 parts of t-butyl peroxy-2-ethylhexanoate. After this mixture was aged for 1 hour, 0.5 parts of t-butyl peroxy-2-ethylhexanoate and 30 parts of xylol were added thereto dropwise over a period of 30 minutes, and the resulting mixture was aged for 2 hours. Thereto was then added 100 parts of the silicone-modified acrylic resin solution synthesized in Production Example 2. Thus, a mixed solution of a hydroxyl group-containing acrylic resin and a silicone-modified acrylic resin was obtained.



PRODUCTION EXAMPLE 27 (Synthesis of Mixed Solution of Hydroxyl Group-Containing Acrylic Resin Containing Sodium Salt and Silicone-Modified Acrylic Resin Containing Sodium Salt)

The mixed solution of a hydroxyl group-containing acrylic resin and a silicone-modified acrylic resin which had been synthesized in Production Example 26 was treated in the same manner as in Production Example 6. Thus, a mixed solution of a hydroxyl group-containing acrylic resin containing a sodium salt and a silicone-modified acrylic resin containing a sodium salt was obtained.

PRODUCTION EXAMPLE 28 (Synthesis of Mixed Solution of Silicone Compound, Hydroxyl Group-Containing Acrylic Resin, and Silicone-Modified Acrylic Resin)

To a reaction mixture containing 70 parts of xylol and maintained at 110°C was added dropwise over a period of 3 hours a solution containing 10 parts of methacrylic acid, 20 parts of 2-hydroxyethyl methacrylate, 25 parts of 2-ethylhexyl methacrylate, 25 parts of t-butyl methacrylate, and 2 parts of t-butyl peroxy-2-ethylhexanoate. After this mixture was aged for 1 hour, 0.5 parts of t-butyl peroxy-2-ethylhexanoate and 30 parts of xylol were added thereto dropwise over a period of 30 minutes, and the resulting mixture was aged for 2 hours. Thereto were then added 100 parts of the silicone-modified acrylic resin solution synthesized in Production Example 2 and 20 parts of the



silicone compound represented by the average composition formula (7) described above. Thus, a mixed solution of a silicone compound, a hydroxyl group-containing acrylic resin, and a silicone-modified acrylic resin was obtained.

PRODUCTION EXAMPLE 29 (Synthesis of Mixed Solution of Silicone Compound, Hydroxyl Group-Containing Acrylic Resin Containing Sodium Salt, and Silicone-Modified Acrylic Resin Containing Sodium Salt)

The mixed solution of a silicone compound, a hydroxyl group-containing acrylic resin, and a silicone-modified acrylic resin which had been synthesized in Production Example 28 was treated in the same manner as in Production Example 6. Thus, a mixed solution of a silicone compound, a hydroxyl group-containing acrylic resin containing a sodium salt, and a silicone-modified acrylic resin containing a sodium salt was obtained.

EXAMPLES 1 TO 16

With 4 parts of urethane resin crosslinking agent "DN-950" (manufactured by Dai-Nippon Ink & Chemicals, Inc.) was mixed 18 parts of the silicone-modified acrylic resins containing a metal salt or an amine salt which had been synthesized in Production Examples 6 to 21. Thus, a coating resin composition was prepared. Thereto was added 4 parts of xylol to prepare a paint. This paint was applied on a glass plate, and the coated glass plate was allowed to stand at room temperature for one week to obtain a crosslinked film.



EXAMPLE 17

With 4 parts of urethane resin crosslinking agent "DN-950" (manufactured by Dai-Nippon Ink & Chemicals, Inc.) was mixed 18 parts of the sodium salt-containing acrylic resin synthesized in Production Example 23. Thus, a coating resin composition was prepared. Thereto was added 4 parts of xylol to prepare a paint. This paint was applied on a glass plate, and the coated glass plate was allowed to stand at room temperature for one week to obtain a crosslinked film.

EXAMPLE 18

With 4 parts of urethane resin crosslinking agent "DN-950" (manufactured by Dai-Nippon Ink & Chemicals, Inc.) was mixed 18 parts of the sodium salt-containing silicone-modified acrylic resin synthesized in Production Example 25. Thus, a coating resin composition was prepared. Thereto was added 4 parts of xylol to prepare a paint. This paint was applied on a glass plate, and the coated glass plate was allowed to stand at room temperature for one week to obtain a crosslinked film.

EXAMPLE 19

With 4 parts of urethane resin crosslinking agent "DN-950" (manufactured by Dai-Nippon Ink & Chemicals, Inc.) was mixed 18 parts of the mixed solution of a sodium salt-containing hydroxyl group-containing acrylic resin and a sodium salt-containing silicone-modified acrylic resin which had been synthesized in Production Example 27. Thus, a



coating resin composition was prepared. Thereto was added 4 parts of xylol to prepare a paint. This paint was applied on a glass plate, and the coated glass plate was allowed to stand at room temperature for one week to obtain a crosslinked film.

EXAMPLE 20

With 4 parts of urethane resin crosslinking agent "DN-950" (manufactured by Dai-Nippon Ink & Chemicals, Inc.) was mixed 18 parts of the mixed solution of a silicone resin, a sodium salt-containing hydroxyl group-containing acrylic resin, and a sodium salt-containing silicone-modified acrylic resin which had been synthesized in Production Example 29. Thus, a coating resin composition was prepared. Thereto was added 4 parts of xylol to prepare a paint. This paint was applied on a glass plate, and the coated glass plate was allowed to stand at room temperature for one week to obtain a crosslinked film.

COMPARATIVE EXAMPLES 1 TO 4

Using the silicone-modified acrylic resins synthesized in Production Examples 2 to 5, crosslinked films were obtained in the same manner as in the Example 1.

TESTS

The crosslinked films obtained in the above examples and comparative examples were subjected to a rubbing test, measurement of contact angle with water, an anti-pollution test, and an accelerated weathering test. The test and

measurement methods are as follows. The results obtained are shown in Table 1.

[Rubbing Test]

Xylol was rubbed against each film forward and backward 100 times in an ordinary manner, and the state of the resulting film surface was visually evaluated based on the following criteria.

- ⊙: no abnormality.
- : almost no abnormality.
- △: film surface slightly blushed.
- ×: film surface blushed.

[Contact Angle with Water]

A 0.2-cc water droplet was dropped onto each film at room temperature, and the contact angle of the film with the water droplet was measured at 1 minute after dropping.

[Anti-pollution Test]

The films were subjected to weathering at the weathering test area in Nippon Paint Co., Ltd., Neyagawa Jigyō-sho for the 2 years of from March 1991 to March 1993 to examine the contamination of the films. The degree of contamination was evaluated by determining the maximum and average of ΔE values using a color-difference meter. Criteria for the evaluation are as follows.

- ⊙: no contamination.
- : almost no contamination.
- △: slight contamination.



x: contamination.

xx: considerable contamination.

[Accelerated Weathering Test]

The films were subjected to 2,000-hour irradiation in a sunshine weather-ometer to visually evaluate the state of each resulting film surface. Further, 60° specular surface gloss was also measured, and the retention of gloss (%) after irradiation based on the gloss measured before irradiation was determined. The visual evaluation was made based on the following criteria.

⊙: no abnormality.

○: almost no abnormality.

△: chalking occurred partly.

×: chalking occurred considerably.

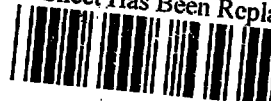


Table 1

		Example																				Comparative Example			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	1	2	3	4
Production Example No.		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	23	25	27	29	2	3	4	5
Rubbing Test		●	●	●	●	○	○	○	○	○	○	○	○	●	●	●	●	●	●	○	○	●	●	●	●
Contact Angle with Water (°C)		58	57	55	60	57	54	58	58	56	55	58	56	58	60	60	59	58	56	62	60	88	86	89	91
Anti-pollution Test		●	○	●	△	○	○	△	△	●	○	○	○	△	△	△	△	●	○	○	○	xx	xx	xx	xx
Accelerated Weathering Test	Glass retention (%)	88	87	90	84	87	87	85	84	88	86	86	85	82	82	83	83	88	84	83	83	78	75	73	75
	Film surface state	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	△	△

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

The coating resin composition of the present invention can form a film having improved anti-pollution properties with maintaining film properties generally required, e.g., weather resistance, because the composition comprises the silicone compound, hydroxyl group-containing resin, and crosslinking agent described hereinabove and because at least part of the functional groups contained in at least one of the silicone compound and the hydroxyl group-containing resin is present in the form of a salt.

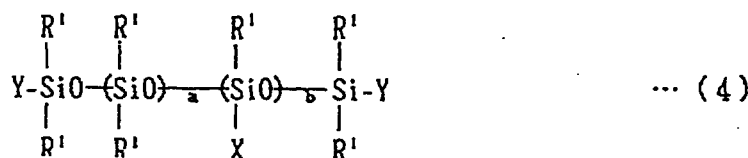
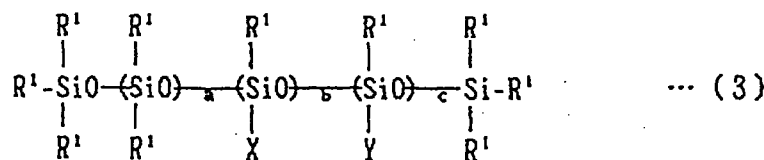
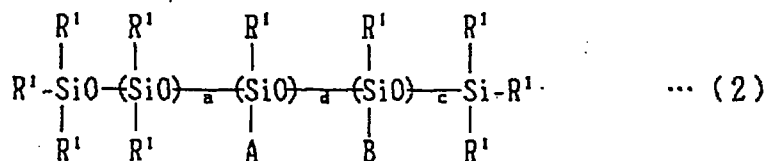
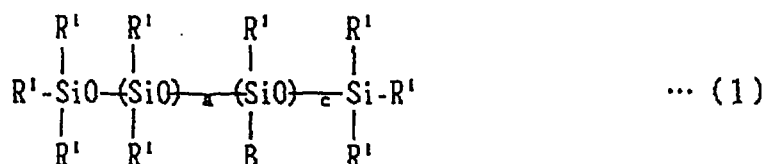
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.





WHAT IS CLAIMED IS:

1. A coating resin composition, which comprises
 at least one silicone compound (A) selected from the
 group consisting of the silicone compounds represented by
 average composition formulae (1), (2), (3), and (4),
 a hydroxyl group-containing resin (B), and
 a crosslinking agent (C) having a functional group
 reactive with a hydroxyl group,
 at least part of the functional groups contained in
 at least one of said silicone compound and said hydroxyl
 group-containing resin being present in the form of a salt;

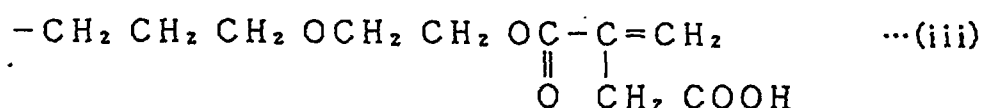
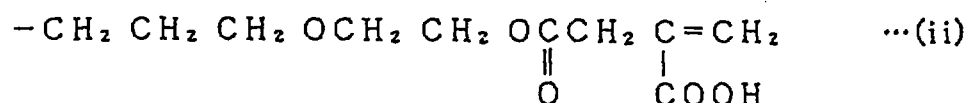
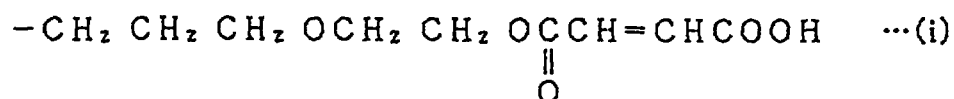


wherein A represents at least one organic residue selected





from the group consisting of the organic residues represented by chemical formulae (i), (ii), and (iii):



B represents $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$,

X represents a 3-acryloxypropyl group or a 3-methacryloxypropyl group,

Y represents a monovalent substituent containing at least one group selected from the group consisting of $-\text{COOH}$, $-\text{SO}_3\text{H}$, and $-\text{NR}_2^1$ (wherein R^2 is an organic residue),

R^1 is an aryl group, an aralkyl group, or an alkyl group having 1 to 6 carbon atoms, and

a, b, c, and d each are the following repeating-unit numbers:

$$1 \leq a \leq 20$$

$$0.5 \leq b \leq 3$$

$$1 \leq c \leq 10$$

$$0 < d \leq 6.$$

2. The coating resin composition as claimed in claim 1, wherein a part of the silicone compound is bonded to a part of the hydroxyl group-containing resin to form a





silicone-modified resin.

3. The coating resin composition as claimed in claim 1, wherein all of the silicone compound is bonded to a part of the hydroxyl group-containing resin to form a silicone-modified resin.

4. The coating resin composition as claimed in claim 1, wherein the hydroxyl group-containing resin has a hydroxyl value of from 20 to 300.

5. The coating resin composition as claimed in claim 1, wherein the mixing ratio ((A):(B)) of the silicone compound (A) to the hydroxyl group-containing resin (B) is from 3:97 to 70:30 by weight.

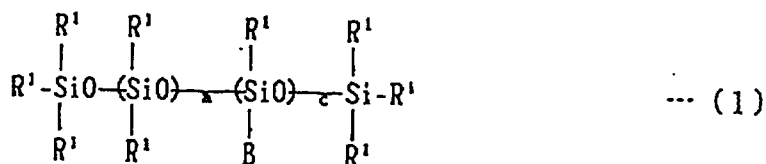
6. A method of applying a paint comprising a coating resin composition which comprises

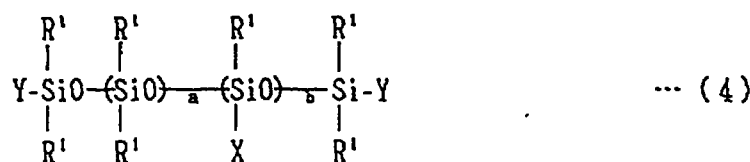
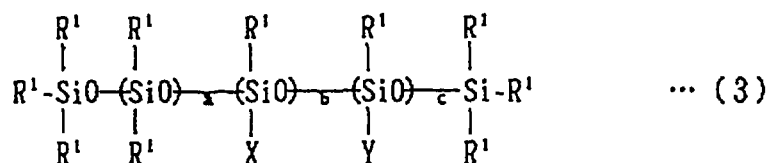
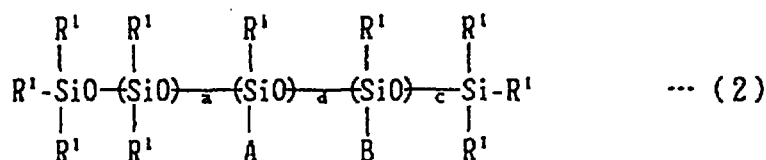
at least one silicone compound (A) selected from the group consisting of the silicone compounds represented by average composition formulae (1), (2), (3), and (4),

a hydroxyl group-containing resin (B), and

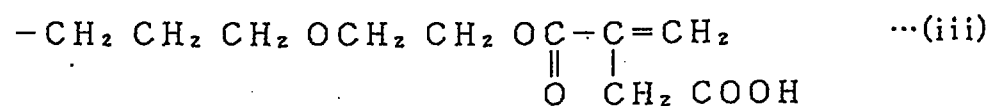
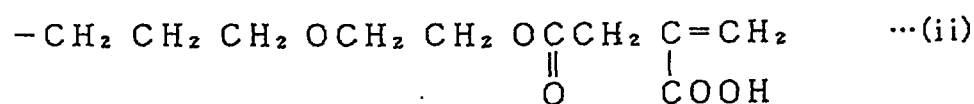
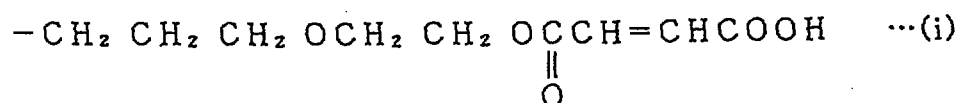
a crosslinking agent (C) having a functional group reactive with a hydroxyl group,

at least part of the functional groups contained in at least one of said silicone compound and said hydroxyl group-containing resin being present in the form of a salt;



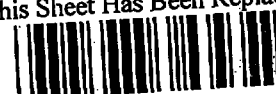


wherein A represents at least one organic residue selected from the group consisting of the organic residues represented by chemical formulae (i), (ii), and (iii):



B represents $-CH_2CH_2CH_2OCH_2CH_2OH$,

X represents a 3-acryloxypropyl group or a 3-methacryloxypropyl group,



THIS SHEET HAS BEEN
REPLACED



Y represents a monovalent substituent containing at least one group selected from the group consisting of $-\text{COOH}$, $-\text{SO}_3\text{H}$, and $-\text{NR}_2^2$ (wherein R^2 is an organic residue), R^1 is an aryl group, an aralkyl group, or an alkyl group having 1 to 6 carbon atoms, and a, b, c, and d each are the following repeating-unit numbers:

$$1 \leq a \leq 20$$

$$0.5 \leq b \leq 3$$

$$1 \leq c \leq 10$$

$$0 < d \leq 6.$$

This Sheet Has Been Replaced

