

DESCRIPTION

GRAFT COPOLYMER CONTAINING POLYORGANOSILOXANE, RESIN
COMPOSITION CONTAINING THE SAME AND PROCESS FOR
5 PREPARING EMULSION OF POLYORGANOSILOXANE

TECHNICAL FIELD

The present invention relates to a flame-retardant resin composition. More specifically, the present invention relates to a graft
10 copolymer containing polyorganosiloxane and a resin composition containing the same, which is excellent in flame retardancy and impact resistance. Also, the present invention relates to a process for preparing an emulsion of polyorganosiloxane.

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BACKGROUND ART

Polycarbonate resin is widely used for electric and electronic parts, OA instruments, household products and building material, due to excellent impact resistance, heat resistance and electric properties. Polycarbonate resin has higher flame retardancy than polystyrene
20 resin. Some fields, particularly the fields of electric and electronic parts and OA instruments, require high flame retardancy and improvement thereof is attempted, by adding various flame retardants. For example, conventionally, organic halogen compounds or organic phosphorous compounds have been added. However, many organic
25 halogen compounds and organic phosphorous compounds are problematic in terms of toxicity and particularly, organic halogen compounds have the problem of producing corrosive gas when burning.

Therefore, demands for achieving flame retardancy by a non-halogen or non-phosphorous flame retardant have been increasing in recent years.

As a non-halogen or non-phosphorous flame retardant, use of a polyorganosiloxane compound (also referred to as silicone) has been suggested. Conventionally, as a method for obtaining an flame-retardant resin composition using a polyorganosilxane compound, known are the method of obtaining flame-retardant resin by kneading a silicone resin comprising monoorganopolysiloxane with a non-silicone polymer (JP-A-54-36365), the method of obtaining a flame-retardant resin composition by dispersing a silicone resin, prepared by mixing 100 parts by weight of polyorganosiloxane and 10 to 150 parts by weight of a silica filler, in a thermoplastic resin (JP-A-8-113712) and the method of obtaining a flame-retardant resin composition by adding a silicone resin, which has a weight average molecular weight of at least 10,000 to at most 270,000 and is soluble in a solvent, to a non-silicone resin containing an aromatic ring (JP-A-10-139964). However, although silicone resin is recognized to have the effect of imparting flame retardancy, the effect is insufficient. When the amount of silicone resin is increased to compensate this insufficiency, impact resistance of the resin composition becomes poor and there is the problem that obtaining a flame-retardant resin composition excellent in both flame retardancy and impact resistance is difficult.

As a method for obtaining a flame-retardant resin composition having impact resistance using a polyorganosiloxane compound, known are the method of obtaining a flame-retardant resin

composition by compounding a composite rubber flame retardant, obtained by graft polymerizing a vinyl monomer to a composite rubber comprising polyorganosiloxane rubber and polyalkyl(meth)acrylate rubber, in a thermoplastic resin (JP-A-2000-17029), the method of
5 obtaining a flame-retardant resin composition by compounding a polyorganosiloxane flame retardant, obtained by grafting a vinyl monomer to composite particles of polyorganosiloxane having an aromatic group and a vinyl monomer, in a thermoplastic resin (JP-A-2000-226420), the method of obtaining a flame-retardant resin
10 composition by compounding a graft copolymer containing polyorganosiloxane, obtained by graft polymerizing a vinyl monomer to polyorganosiloxane particles of at most 0.2 μm , in a thermoplastic resin (JP-A-2000-264935) and the method of obtaining a flame-retardant resin composition by compounding respectively a
15 specific amount of a graft copolymer containing polyorganosiloxane, obtained by graft polymerizing a vinyl monomer to polyorganosiloxane particles of at most 0.2 μm , and polytetrafluoroethylene in a thermoplastic resin (JP-A-2002-348453). However, although each flame-retardant resin composition has impact resistance of a
20 satisfactory level, flame retardancy of a sufficient level cannot be obtained in a thin molded article, for which demands are increasing in the market, and significant improvement in flame retardancy is desired.

Usually, in emulsion polymerization of cyclic siloxane under
25 the condition of an acid catalyst, polymerization conversion ratio is known to be approximately 85 % and improvement in polymerization conversion ratio is desired (see for example USP 532,471 or "Silicone"

published by The Nippon Kogyo Shimbun, Ltd., February 2, 1974, p. 38).

Also, in recent years, pollution due to residue of siloxane of low molecular weight in polyorganosiloxane resin and influence of cyclic siloxane of low molecular weight to the environment is a problem and keeping the residue of low molecular weight siloxane as low as possible is becoming necessary.

On the other hand, as a method of emulsion polymerization of polyorganosiloxane, known is the process for preparing an emulsion of polyorganosiloxane obtained from polyorganopolysiloxane and organosilane having a condensation reactive group, which can be bonded with a silicone atom, or a partially hydrolyzed condensate thereof.

For example, known are the method of emulsion polymerizing cyclic organosiloxane and organotrialkoxysilane bonded with a functional group (JP-B-56-38609) and the method of adding alkoxysilanes having 3 to 4 functional groups as a crosslinking agent when polymerizing siloxane (JP-A-60-252613). Also, in another document (JP-A-61-106614), described is a process for preparing an emulsion of polyorganosiloxane, which comprises adding alkoxysilanes having 2 to 4 functional groups as a crosslinking agent in the presence of organopolysiloxane. More specifically, described is the process for emulsion polymerizing cyclic or linear siloxane of low molecular weight and a crosslinking agent, in the presence of 1 to 50 % by weight, preferably 10 to 30 % by weight, of polysiloxane as a pre-polymerized latex.

The above methods are methods for coexisting compounds

having a hydrolyzable silicone functional group (alkoxysilane) excluding cyclic siloxane in emulsion polymerization. By coexisting multi-functional alkoxysilane as a component of siloxane having low molecular weight when polymerizing polysiloxane, unwanted
5 condensation reaction among the crosslinking agent progresses when polymerizing and by-products such as scale particles are produced. As a result, there is concern that the properties may be adversely affected. Also, polymerization conversion ratio is insufficient and a method for improving polymerization conversion ratio further is
10 desired.

DISCLOSURE OF INVENTION

The present invention relates to a graft copolymer containing polyorganosiloxane obtained by 0 to 10 parts by weight of a
15 vinyl monomer (B) comprising 100 to 20 % by weight of a multi-functional monomer containing at least two polymerizable unsaturated bonds in a molecule (b-1) and 0 to 80 % by weight of another copolymerizable monomer (b-2) and 5 to 70 parts by weight of a vinyl monomer (C), in the presence of 30 to 95 parts by weight of
20 polyorganosiloxane in a latex state (A), so that the total amount of polyorganosiloxane (A), vinyl monomer (B) and vinyl monomer (C) becomes 100 parts by weight.

Polyorganosiloxane (A) is preferably obtained by seed polymerizing organosiloxane using a seed polymer that is swelled by
25 organosiloxane.

The particle size of the seed polymer is preferably 0.001 to 0.03 μm .

T_g (glass transition temperature) of the seed polymer is preferably at most 0°C.

The proportion of the seed polymer to polyorganosiloxane (A) is preferably 0.1 to 10 % by weight.

5 The swelling volume ratio of the seed polymer is preferably 3 to 50 times.

The swelling volume ratio is preferably 5 to 25 times.

○ The vinyl monomer (C) is preferably at least one monomer selected from the group consisting of an aromatic vinyl monomer, a
10 cyanized vinyl monomer, a (meth)acrylic ester monomer and a vinyl monomer containing a carboxyl group.

A radical polymerization initiator (D) having solubility to water of 0.5 to 10 g/100 g (20°C) and hydrogen drawing properties of 10 to 30 % is preferably used when polymerizing vinyl monomer (B)
15 and/or vinyl monomer (C).

Polyorganosiloxane (A) is preferably modified by a grafting agent (E).

○ The amount of grafting agent (E) is preferably 0.1 to 10 parts by weight based on 100 parts by weight of polyorganosiloxane
20 (A).

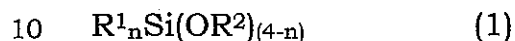
Polyorganosiloxane (A), which is modified by grafting agent (E), is preferably reacted with grafting agent (F) and then vinyl monomer (B) and vinyl monomer (C) are preferably polymerized.

The reaction temperature of grafting agent (F) and vinyl
25 monomer (B) is preferably 20 to 60°C.

The present invention also relates to a flame retardant comprising the graft copolymer containing polyorganosiloxane.

The present invention also relates to a resin composition comprising 0.1 to 20 parts by weight of the flame retardant based on 100 parts by weight of thermoplastic resin.

The present invention also relates to a process for preparing
5 an emulsion of polyorganosiloxane, which comprises obtaining polyorganosiloxane (H) by emulsion polymerizing cyclic organosiloxane under acidic conditions of pH of at most 5, and adding condensation reactive organosilane represented by formula (1):



(wherein R^1 represents an organic group, R^2 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, n represents an integer of 0 to 3) or a partially hydrolyzed condensate thereof (I)
15 (hereinafter referred to as condensation reactive organosilane (I)).

0.1 to 50 parts by weight of condensation reactive organosilane (I) is preferably added based on 100 parts by weight of polyorganosiloxane (H) and reaction is preferably conducted at a temperature of 30 to 95°C under acidic conditions of pH of at most 5.

20 The temperature of polyorganosiloxane (H) when adding condensation reactive organosilane (I) is preferably 10 to 50°C.

Polyorganosiloxane (H) is preferably obtained by polymerizing 100 parts by weight of cyclic organosiloxane and 0.01 to 20 parts by weight an alkoxysilane compound having a
25 radical-polymerizable functional group in a molecule (J).

Polyorganosiloxane (H) is preferably obtained by emulsion polymerizing under acidic conditions and then aging at a temperature

of 10 to 50°C for at least 6 hours.

The radical-polymerizable functional group of alkoxysilane compound (J) is preferably at least one functional group selected from the group consisting of a (meth)acryloyloxy group, a mercapto group, a vinyl group and a styryl group.

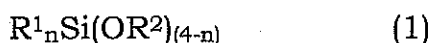
The present invention also relates to a graft copolymer containing polyorganosiloxane obtained by polymerizing 5 to 70 parts by weight of a vinyl monomer based on 95 to 30 parts by weight of polyorganosiloxane particles in the emulsion of polyorganosiloxane obtained by the above process, so that the total amount becomes 100 parts by weight.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention relates to a graft copolymer containing polyorganosiloxane obtained by polymerizing 0 to 10 parts by weight of a vinyl monomer (B) comprising 100 to 20 % by weight of a multi-functional monomer containing at least two polymerizable unsaturated bonds in a molecule (b-1) and 0 to 80 % by weight of another copolymerizable monomer and 5 to 70 parts by weight of a vinyl monomer (C), in the presence of 30 to 95 parts by weight of polyorganosiloxane in a latex state (A), so that the total amount of polyorganosiloxane (A), vinyl monomer (B) and vinyl monomer (C) becomes 100 parts by weight.

Polyorganosiloxane (A) used in the present invention can be obtained by normal emulsion polymerization, but is preferably obtained by seed polymerizing organosiloxane using a seed polymer that is swelled by organosiloxane, from the viewpoint of advantages

such as particle size distribution in latex can be made narrow and flame retardancy is favorable. Also, as polyorganosiloxane (A), a substance obtained by obtaining polyorganosiloxane (H) by emulsion polymerizing cyclic organosiloxane under acidic conditions of pH of at most 5 and then adding condensation reactive organosilane represented by formula (1):



(wherein R^1 represents an organic group, R^2 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, n represents an integer of 0 to 3) is preferably used, as described later, from the viewpoints of being easily obtainable and cost.

The seed polymer can be any seed polymer that swells when organosiloxane is added and does not need to be hydrophilic. The seed polymer can be obtained by normal emulsion polymerization and the synthesizing process is not particularly limited. Examples of the seed polymer that is swelled by organosiloxane are not limited to rubber components such as butyl acrylate rubber, butadiene rubber, butadiene-styrene rubber and butadiene-acrylonitrile rubber and polymers such as a copolymer of butyl acrylate and styrene and a copolymer of styrene and acrylonitrile can be used. Also, a chain transfer agent is not used for polymerization of the seed polymer and so the seed polymer does not have water solubility.

To improve swellability of the seed polymer to organosiloxane, the method of lowering T_g of the seed polymer and the method of decreasing the particle size of the seed polymer are effective. Particularly, the latter is extremely effective. T_g of the seed polymer is

preferably at most 0°C, more preferably at most -20°C. The particle size of the seed polymer in a latex state is preferably 0.001 to 0.03 μm, more preferably 0.005 to 0.01 μm. When the particle size is within the above range, the seed polymer can easily be synthesized with stability and has favorable swellability. Also, flame retardancy of the final molded article is improved.

Swellability of the seed polymer is preferably 3 to 50 times, more preferably 5 to 25 times, in swelling volume ratio. When the swelling volume ratio is less than 3 times, the effect of improving flame retardancy of the final molded article is small and when the swelling volume ratio is more than 50 times, synthesizing the seed polymer is difficult.

Herein, the swelling volume ratio is the value found from the ratio of particle size of the seed polymer in latex before swelling with organosiloxane and the latex particle size, after adding organosiloxane in an amount of 50 times (by weight) the solid content of the seed polymer to latex of the seed polymer and then stirring for 1 hour at 23°C. The swelling volume ratio is found from the following equation:

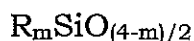
Swelling volume ratio =

$$(\text{particle size after swelling} / \text{particle size before swelling})^3 - 1$$

The seed polymer is preferably used in an amount of 0.1 to 10 % by weight, more preferably 0.5 to 3 % by weight based on polyorganosiloxane (A). When the amount of the seed polymer is less than 0.1 % by weight, the polymerization time becomes extremely long

and the particle size of the obtained polyorganosiloxane (A) becomes too large that flame retardancy and impact resistance of the final molded article tends to decrease. When the amount of the seed polymer is more than 10 % by weight, flammable components other than polyorganosiloxane increase in the particles of polyorganosiloxane (A) and as a result, flame retardancy of the final molded article tends to decrease.

Organosiloxane used for polymerization of polyorganosiloxane (A) has a structure unit represented by the formula:



(wherein R represents a substituent or non-substituent monovalent hydrocarbon group, m represents an integer of 0 to 3) and has a linear, branched or cyclic structure. Preferably, the organosiloxane has a cyclic structure. Examples of the substituent or non-substituent monovalent hydrocarbon group of the organosiloxane are a methyl group, an ethyl group, a propyl group, a phenyl group and a substituent hydrocarbon group wherein the hydrogen atom of the above are substituted with a cyano group.

Examples of the organosiloxane are cyclic compounds such as hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6) and trimethyltriphenylcyclotrisiloxane and linear or branched organosiloxane. These organosiloxane can be used alone or two or more kinds can be used together.

In polymerization of polyorganosiloxane (A) used in the present invention, grafting agent (E) can be used. Modifying polyorganosiloxane (A) by grafting agent (E) is preferable from the viewpoint of efficiently graft polymerizing vinyl monomer (B) and vinyl
5 monomer (C).

Examples of grafting agent (E) that can be used in the present invention are p-vinylphenylmethyldimethoxysilane, p-vinylphenylethyldimethoxysilane, 2-(p-vinylphenyl)ethyldimethoxysilane,
10 3-(p-vinylbenzoyloxy)propylmethyldimethoxysilane, vinylmethyldimethoxysilane, tetravinyltetramethylcyclsiloxane, allylmethyldimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane. At least one of these can be selected accordingly and used.

15 The proportion of grafting agent (E) that is used is preferably 0.1 to 10 % by weight, more preferably 1 to 8 % by weight, further preferably 2 to 6 % by weight based on organosiloxane. When the amount of grafting agent (E) is too large, flame retardancy and impact resistance of the final molded article tend to decrease. When
20 the amount of grafting agent (E) is too small, moldability of the final molded article tends to decrease.

When synthesizing polyorganosiloxane (A) used in the present invention, a crosslinking agent can be used when necessary. Examples of the crosslinking agent are trifunctional crosslinking
25 agents such as methyltrimethoxysilane, phenyltrimethoxysilane and ethyltriethoxysilane and tetrafunctional crosslinking agents such as tetraethoxysilane, 1,3-bis[2-(dimethoxymethylsilyl)ethyl]benzene,

1,4-bis[2-(dimethoxymethylsilyl)ethyl]benzene,
1,3-bis[1-(dimethoxymethylsilyl)ethyl]benzene,
1,4-bis[1-(dimethoxymethylsilyl)ethyl]benzene,
1-[1-(dimethoxymethylsilyl)ethyl]-3-[2-(dimethoxymethylsilyl)ethyl]benz
5 ene and
1-[1-(dimethoxymethylsilyl)ethyl]-4-[2-(dimethoxymethylsilyl)ethyl]benz
ene. These crosslinking agents can be used alone or two or more
kinds can be mixed and used. The amount of the crosslinking agent
that is added is preferably at most 10 % by weight, more preferably at
10 most 3.0 % by weight based on polyorganosiloxane (A). When the
amount is more than 10 % by weight, flexibility of polyorganosiloxane
(A) is lost and impact resistance of the final molded article tends to
decrease.

The average particle size of polyorganosiloxane (A) is
15 preferably 0.008 to 0.6 μm , more preferably 0.1 to 0.3 μm . Obtaining
polyorganosiloxane having average particle size of less than 0.008 μm
with stability may be difficult and when the average particle size is
more than 0.6 μm , flame retardancy and impact resistance of the final
molded article tend to become poor.

20 Vinyl monomer (B) used in the present invention is a
component used for improving flame retardancy and impact resistance
and comprises 100 to 20 %, preferably 100 to 50 %, more preferably
100 to 80 % of a multi-functional monomer containing at least two
polymerizable unsaturated bonds in a molecule (b-1) and 0 to 80 %,
25 preferably 0 to 50 %, more preferably 0 to 20 % of another
copolymerizable monomer (b-2).

When the amount of the multi-functional monomer (b-1) is

too small or the amount of the copolymerizable monomer (b-2) is too large, in both cases, the effect of improving impact resistance of the graft copolymer that is ultimately obtained tends to become low.

Examples of the multi-functional monomer (b-1) are allyl
5 methacrylate, ethylene glycol dimethacrylate, 1,3-butyleneglycol dimethacrylate and divinylbenzene. These may be used alone or two or more kinds can be used together.

Examples of the other copolymerizable monomer (b-2) are aromatic vinyl monomers such as styrene and α -methylstyrene;
10 cyanized vinyl monomers such as acrylonitrile and (meth)acrylic ester monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate. These may be used alone or two or more kinds can be used together.

Vinyl monomer (C) used in the present invention is a
15 component used for acquiring solubility between the graft copolymer and thermoplastic resin, to homogeneously disperse the graft copolymer in thermoplastic resin. Vinyl monomer (C) is not particularly limited, but specific examples are aromatic vinyl monomers such as styrene and α -methylstyrene; cyanized vinyl
20 monomers such as acrylonitrile, (meth)acrylic ester monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate and vinyl monomers containing a carboxyl group such as itaconic acid, (meth)acrylic acid, fumaric acid and maleic acid. These may be used alone or two or
25 more kinds can be used together. Particularly, vinyl monomer (C) is preferably at least one monomer selected from the group consisting of an aromatic vinyl monomer, a cyanized vinyl monomer, a (meth)acrylic

ester monomer and a vinyl monomer containing a carboxyl group, from the viewpoints of being easily available and cost.

The present invention is preferably obtained by polymerizing 0 to 10 parts by weight, preferably 1 to 8 parts by weight, of vinyl monomer (B) and 5 to 70 parts by weight, preferably 10 to 50 parts by weight, of vinyl monomer (C), in the presence of 30 to 95 parts by weight, preferably 50 to 90 parts by weight, of polyorganosiloxane (A), so that the total amount of polyorganosiloxane (A), vinyl monomer (B) and vinyl monomer (C) becomes 100 parts by weight.

When the amount of polyorganosiloxane (A) is less than 30 parts by weight, sufficient flame retardancy and impact resistance cannot be obtained in the final molded article and when the amount is more than 95 parts by weight, flame retardancy, impact resistance, and apperance of the final molded article become poor. When the amount of vinyl monomer (B) is more than 10 parts by weight, impact resistance of the final molded articles decreases. When the amount of vinyl monomer (C) is less than 5 parts by weight, appearance, flame retardancy and impact resistance of the final molded article decrease and when the amount is more than 70 parts by weight, flame retardancy and impact resistance of the final molded article decrease.

Also, the graft copolymer containing polyorganosiloxane is preferably obtained by reacting 30 to 94.9 parts by weight of polyorganosiloxane (A) modified by grafting agent (E) with 0.1 to 10 parts by weight of grafting agent (F) and then polymerizing 5 to 70 parts by weight of vinyl monomer (C), so that the amount of polyorganosiloxane (A), grafting agent (F) and vinyl monomer (C) becomes 100 parts by weight in total. In a more preferable

embodiment, 30 to 94.9 parts by weight of polyorganosiloxane (A) modified by grafting agent (E) is reacted with 0.1 to 10 parts by weight of grafting agent (F), 0 to 10 parts by weight of vinyl monomer (B) comprising 100 to 20 % by weight of a multi-functional monomer
5 containing at least two polymerizable unsaturated bonds in a molecule (b-1) and 0 to 80 % by weight of another copolymerizable monomer (b-2) is reacted at least one step and then 5 to 70 parts by weight of vinyl monomer (C) is polymerized. In a further preferable embodiment, neutralization is conducted after vinyl monomer (B) is reacted. In an
10 even more preferable embodiment, after neutralization, 0 to 10 parts by weight of vinyl monomer (G) comprising 100 to 20 % by weight of a multi-functional monomer containing at least two polymerizable unsaturated bonds in a molecule (g-1) and 0 to 80 % by weight of another copolymerizable monomer (g-2) is reacted at least one step and
15 then 5 to 70 parts by weight of vinyl monomer (C) is polymerized.

As grafting agent (F), the same grafting agents as those used for grafting agent (E) can be used.

Grafting agent (E) is copolymerized with organosiloxane, a difunctional silane compound or a silane compound having at least 3
20 functional groups and is a component for introducing a vinyl polymerizable group in a side chain or a terminal of the copolymer. The vinyl polymerizable group functions as a graft activity point when chemically bonding with a vinyl (co)polymer comprising vinyl monomer (B) and/or vinyl monomer (C) and/or vinyl monomer (G). Furthermore,
25 the activity points can be radically reacting by a radical polymerization initiator to form crosslinked bonds and grafting agent (E) is a component that can be used as a crosslinking agent. Therefore, the

total amount of grafting agent (E) and grafting agent (F) that is used is preferably 0.1 to 10 % by weight, more preferably 0.5 to 5 % by weight based on organosiloxane particles. When the total amount of grafting agent (E) and grafting agent (F) is more than 10 % by weight, crosslinked bonds are excessively formed and flame retardancy and impact resistance of the final molded article may decrease. On the other hand, when the total amount of grafting agent (E) and grafting agent (F) is less than 0.1 % by weight, graft activity points decrease and flame retardancy and moldability of the final molded article may decrease.

Conventionally, all of the grafting agent was mixed when polymerizing polyorganosiloxane. By dividing and adding part (grafting agent (E)) of the grafting agent and then, after the polymerization conversion ratio of polyorganosiloxane reaches equilibrium, adding and reacting the remaining part (grafting agent (F)) of the grafting agent to the latex under conditions in which ring-opening polymerization of polyorganosiloxane has difficulty progressing, the final molded article exhibits high flame retardancy while maintaining high impact resistance.

The reason for this is speculated to be that by adding grafting agent (F) under conditions in which ring-opening polymerization of polyorganosiloxane has difficulty progressing, the rate at which grafting agent (F) is introduced into the particles in equilibrium reaction of polyorganosiloxane decreases and as a result, particles are formed, wherein grafting agent (F) is unevenly distributed on the surface of particles. Consequently, by gathering the grafting agent of the center layer, which conventionally did not function as graft

activity points due to being evenly located inside the polyorganosiloxane particles, to the particle surface, effectively utilizing the function of graft activity points in comparison to the conventional particle is presumed to have been successful. Therefore, the number
5 of effective graft activity points increase while maintaining the total amount of the grafting agent that is used and in the final molded article, flame retardancy is improved while maintaining impact resistance.

The amount of grafting agent (E) when reacting
10 polyorganosiloxane (A) modified by grafting agent (E) with grafting agent (F) is preferably 0.1 to 10 parts by weight, more preferably 1 to 4 parts by weight, in order to obtain 100 parts by weight of modified polyorganosiloxane (A). When the amount of grafting agent (E) is less than 0.1 part by weight, flame retardancy and appearance of the final
15 molded article tend to decrease and when the amount is more than 10 parts by weight, impact resistance tends to decrease.

Modified polyorganosiloxane (A) is obtained by emulsifying organosiloxane and grafting agent (E) in water in the presence of an emulsifier by mechanical shearing and then reacting by acidifying the
20 emulsion.

When grafting agent (F) is directly added to acidic polyorganosiloxane (A), grafting agent (F) reacts with each other before reacting with polyorganosiloxane particles to produce foreign matter, which causes decrease in flame retardancy and impact resistance.
25 Therefore, grafting agent (F) is preferably emulsified in deionized water containing a small amount of an emulsifier in advance and then used.

Also, equilibrium reaction of polyorganosiloxane (A) in an

acidic state changes according to the temperature and the reaction temperature of grafting agent (F) and vinyl monomer (B) is preferably 20 to 60°C, more preferably 30 to 50°C. When the temperature is lower than 20°C, radical polymerization of vinyl monomer (B) does not
5 progress and unreacted monomers increase. When the temperature is higher than 60°C, equilibrium reaction of polyorganosiloxane (A) progresses excessively, effective graft activity points decrease and the effect of improving flame retardancy may not be sufficiently obtained.

When the latex is left for a long period of time in an acidic
10 state, the grafting agent on the particle surface is decreased due to equilibrium reaction. Therefore, immediately after the reaction is finished, neutralization is preferably conducted by adding an alkali aqueous solution of sodium hydroxide, potassium hydroxide and sodium carbonate.

15 Also, by polymerizing vinyl monomer (C) after reaction of grafting agent (F) and neutralization, the polymerization ratio of polyorganosiloxane (A) can be improved.

When the grafting agent is used divided into grafting agent (E) and grafting agent (F), the amount of the multi-functional monomer containing at least two polymerizable unsaturated bonds in a molecule
20 (b-1) that constitutes vinyl monomer (B) and the multi-functional monomer containing at least two polymerizable unsaturated bonds in a molecule (g-1) that constitutes vinyl monomer (G) is preferably 100 to 20 % by weight, more preferably 100 to 50 % by weight, particularly
25 preferably 100 to 80 % by weight. Also, the amount of another copolymerizable monomer (b-2) that constitutes vinyl monomer (B) and another copolymerizable monomer (g-2) that constitutes vinyl monomer

(G) is preferably 0 to 80 % by weight, more preferably 0 to 50 % by weight, particularly preferably 0 to 20 % by weight. When the amount of multifunctional monomer (b-1) and multifunctional monomer (g-1) is too small or when the amount of another copolymerizable monomer (b-2) and another copolymerizable monomer (g-2) is too large, in any case, the effect of improving flame retardancy and impact resistance of the ultimately obtained graft copolymer tends to become low.

As multi-functional monomer (g-1) that constitutes vinyl monomer (G), the same monomers as those used for multifunctional monomer (b-1) can be used and as another copolymerizable monomer (g-2) the same monomers as those used for another copolymerizable monomer (b-2) can be used.

With respect to the total amount of vinyl monomer (B) and vinyl monomer (G) that is used based on 100 parts by weight of the polyorganosiloxane particles in polyorganosiloxane (A), the lower limit is preferably at least 1 part by weight and the upper limit is preferably less than 10 parts by weight, more preferably less than 8 parts by weight. When the total amount of vinyl monomer (B) and vinyl monomer (G) is less than 1 part by weight or when the total amount of vinyl monomer (B) and vinyl monomer (G) is more than 10 parts by weight, in both cases, the effect of improving flame retardancy and impact resistance of the ultimately obtained graft copolymer tends to become low. The amount of vinyl monomer (G) when added separately is preferably 1 to 10 parts by weight, more preferably 1 to 3 parts by weight. When the amount is within this range, polymerization ratio of polyorganosiloxane (A) is improved and also, flame retardancy improves, thus being favorable.

When vinyl monomer (B), vinyl monomer (C) and vinyl monomer (G) are used for polymerization, emulsion polymerization can be employed and radical polymerization can be conducted in latex of polyorganosiloxane (A) modified by the grafting agent.

5 Examples of the radical polymerization initiator used when polymerizing vinyl monomer (B), vinyl monomer (C) and vinyl monomer (G) are organic peroxides such as cumene hydroperoxide, t-butyl hydroperoxide, benzoyl peroxide, t-butylperoxyisopropylcarbonate, di-t-butyl peroxide, t-butylperoxylaurate, p-menthane hydroperoxide, 10 t-hexyl hydroperoxide, lauroyl peroxide, succinic acid peroxide, cyclohexanone peroxide and acetylacetone peroxide; inorganic peroxides such as potassium persulfate and ammonium persulfate; and azo compounds such as 2,2'-azobisisobutyronitrile and 2,2'-azobis-2,4-dimethylvaleronitrile. Of these, in view of high 15 reactivity, organic peroxides and inorganic peroxides are preferable.

Also, examples of a reducing agent used in a redox system are mixtures of ferrous sulfate/glucose/sodium pyrophosphate, ferrous sulfate/dextrose/sodium pyrophosphate and ferrous sulfate/sodium formaldehyde sulfoxylate/ethylenediamineacetate.

20 Particularly, a radical polymerization initiator (D) having solubility to water of 0.5 to 10 g/100 g (20°C), more preferably 0.5 to 5 g/100 g (20°C), and hydrogen drawing properties of 10 to 30 %, more preferably 15 to 25 %, is preferable from the viewpoint of efficiently covering polyorganosiloxane (A) by vinyl monomer (C). Examples of 25 radical polymerization (D) are t-hexyl hydroperoxide and p-menthane hydroperoxide.

When the solubility to water of the radical polymerization

initiator at 20°C is lower than 0.5 g/100 g, graft efficiency (= (weight of graft polymer)/(weight of graft monomer)) of the graft copolymer containing polyorganosiloxane becomes high, but graft polymerization occurs inside the polyorganosiloxane particles and the ratio of graft polymerization at the particle surface is presumed to become relatively low. As a result, flame retardancy of the final molded article tends to decrease. When the solubility to water at 20°C is higher than 10 g/100 g, polymerization of the graft monomer occurs in the water phase and as a result, graft efficiency decreases and flame retardancy of the final molded articles decreases.

The hydrogen drawing properties of radical polymerization initiator (D) is measured by the MSD trapping method (Makrol.Chem., 155, 239 (1972)). When the hydrogen drawing properties are lower than 10 %, conversion ratio of graft polymerization has difficulty increasing and flame retardancy of the final molded articles decreases. When the hydrogen drawing properties are more than 30 %, the polymerization rate decreases during graft polymerization and flame retardancy of the final molded articles decreases.

When polymerization using radical polymerization initiator (D) is conducted in a redox system such as ferrous sulfate/sodium formaldehyde sulfoxylate/disodium ethylenediaminetetraacetate, ferrous sulfate/glucose/sodium pyrophosphate and ferrous sulfate/sodium pyrophosphate/sodium phosphate, polymerization is completed even in a low polymerization temperature.

Usually, the amount of radical polymerization initiator (D) that is used is preferably 8×10^{-8} to 4×10^{-3} mol, more preferably 3×10^{-7} to 1×10^{-3} mol, particularly preferably 5×10^{-6} to 2×10^{-4} mol,

based on 1 mol of vinyl monomer (B), vinyl monomer (C) or vinyl monomer (G) that is used. When the amount of radical polymerization initiator (D) is less than 8×10^{-8} mol, the reaction rate is slow and production efficiency tends to become poor. When the amount of
5 radical polymerization initiator (D) is more than 4×10^{-3} mol, heat generation during the reaction becomes large and production tends to become difficult.

The method for separating the graft copolymer from latex of the graft copolymer containing polyorganosiloxane obtained in the
10 above manner is not particularly limited and an example is the method of coagulating by adding a metal salt such as calcium chloride, magnesium chloride and magnesium sulfate to the latex, separating, washing with water, dehydrating and drying the latex. Also, the spray drying method can be used.

15 By compounding in various thermoplastic resins, the graft copolymer containing polyorganosiloxane obtained in this way provides a resin composition excellent in flame retardancy and impact resistance.

As the thermoplastic resin, polycarbonate resin containing
20 at least 50 % by weight of polycarbonate is preferable from the viewpoint that favorable flame retardancy is achieved. Preferable examples of polycarbonate resin are polycarbonate; mixed resin of polycarbonate and polyester such as mixed resin of polycarbonate and polyethylene terephthalate and mixed resin of polycarbonate and
25 polybutylene terephthalate; mixed resin of polycarbonate and acrylonitrile/styrene copolymer; mixed resin of polycarbonate and butadiene/styrene copolymer (HIPS resin); mixed resin of

polycarbonate and acrylonitrile/butadiene rubber-styrene copolymer (ABS resin); mixed resin of polycarbonate and acrylonitrile/butadiene rubber/ α -methylstyrene copolymer; mixed resin of polycarbonate and styrene/butadiene rubber/acrylonitrile/N-phenylmaleimide copolymer
5 and mixed resin of polycarbonate and acrylonitrile/acrylic rubber/styrene copolymer (AAS resin).

With respect to the amount of the graft copolymer containing polyorganosiloxane that is added based on the thermoplastic resin, from the viewpoint of flame retardancy, 0.1 to 20
10 parts by weight, more preferably 0.5 to 10 parts by weight, of the graft copolymer (flame retardant) is preferably compounded based on 100 parts by weight of the thermoplastic resin. When the amount is less than 0.1 part by weight, flame retardancy of the final molded article may not improve. When the amount is more than 20 parts by weight,
15 moldability (particularly flowability) of the molded article may decrease significantly.

The flame retardant powder comprising the graft copolymer containing polyorganosiloxane, which is coagulated, thermally treated, dehydrated and dried from the latex, and the thermoplastic resin can
20 be mixed using a henschel mixer or a ribbon blender and then melting and kneading using a roll, an extruder or a kneader.

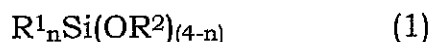
At this time, a compounding agent that is usually used can be compounded, that is an antioxidant, an anti-dropping agent, a polymer processing aid, a flame retardant, an impact modifier, a
25 plasticizer, a lubricant, an ultraviolet ray absorbing agent, a pigment, glass fiber, a filler and a polymer lubricant.

As the method for molding the flame retardant resin

composition, a molding method that is usually used for molding thermoplastic resin can be applied, that is injection molding, extrusion molding, blow molding and calender molding.

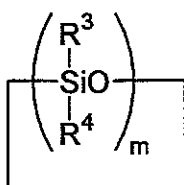
Applications of the molded article obtained from the flame retardant resin composition of the present invention are not particularly limited. Examples are applications which require flame retardancy such as a desktop computer, a laptop computer, a tower computer, a server computer, a printer and a copying machine. The obtained molded article is excellent in flame retardancy and impact resistance.

The present invention also relates to a process for preparing an emulsion of polyorganosiloxane, which comprises obtaining polyorganosiloxane (H) by emulsion polymerizing cyclic organosiloxane under acidic conditions of pH of at most 5 and then adding condensation reactive organosilane represented by formula (1):



(wherein R^1 represents an organic group, R^2 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, n represents an integer of 0 to 3).

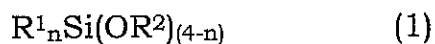
Polyorganosiloxane (H) is obtained by emulsion polymerizing cyclic organosiloxane under acidic conditions of pH of at most 5. Herein, cyclic organosiloxane is preferably represented by the formula:



(wherein R^3 and R^4 respectively represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 8 carbon atoms such as a methyl group, an ethyl group, a propyl group, a butyl group, a vinyl group, an allyl group and a phenyl group, m represents an integer of 3 to 8; in each repeating unit, R^3 and R^4 can be the same or different).

More specifically, examples are hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, 1,1-diethylhexamethylcyclotetrasiloxane, phenylheptamethylcyclotetrasiloxane, 1,1-diphenylhexamethylcyclotetrasiloxane, 1,2,3,4-tetravinyl-1,2,3,4-tetramethylcyclotetrasiloxane, 1,2,3,4-tetrahydro-1,2,3,4-tetramethylcyclotetrasiloxane, dodecamethylcyclohexasiloxane and 1,2,3,4-tetraphenyl-1,2,3,4-tetramethylcyclotetrasiloxane. Of these, octamethylcyclotetrasiloxane is preferable from the viewpoints of being easily available and cost.

The condensation reactive organosilane (I) is a component necessary for improving polymerization conversion ratio. The condensation reactive organosilane (I) in the present invention is not particularly limited as long as the condensation reactive organosilane is condensation reactive organosilane represented by the following formula (1):



25

(wherein R^1 represents an organic group, R^2 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, n represents an

integer of 0 to 3) or a partially hydrolyzed condensate thereof. The composition of formula (1) is described below in further detail.

In the formula, R^1 is not particularly limited as long as R^1 represents any organic group. Specifically, examples are alkyl groups
5 such as a methyl group, an ethyl group and a propyl group and aryl groups such as a phenyl group and a tolyl group.

R^1 can be a radical-polymerizable functional group described above or an alkyl group having the radical-polymerizable functional group. In such a case, condensation reactive organosilane
10 (I) may comprise the same components as the alkoxysilane compound (J) described below. However, adding the same components as alkoxysilane compound (J) as condensation reactive organosilane (I) after conducting polycondensation of polyorganosiloxane (H) and alkoxysilane compound (J) is not particularly a problem, in the case
15 that improvement in polymerization conversion ratio, which is an object of the present invention, is achieved.

In the formula, R^2 is not particularly limited as long as R^2 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms. Herein, condensation reactive group OR^2 in the formula
20 condenses with the silanol terminal of polyorganosiloxane (H) obtained by emulsion polymerization of cyclic organosiloxane. At this time, by reacting condensation reactive organosilane (I) with silanol in the terminal of organosiloxane having low molecular weight under acidic conditions, organosiloxane having low molecular weight can become
25 nonvolatile matter and as a result, polymerization conversion ratio is considered to improve. However, from the viewpoints of selectivity of the reaction and inhibition of production of by-products such as scale

particles, the condensation reactive group is preferably an alkyl group having 1 to 5 carbon atoms, more preferably 2 to 4 carbon atoms. When the number of carbon atoms is small, hydrolysis properties are high, selectivity of the reaction is low and scale particles may be produced. However, in the case that R^1 is an aryl group, because
5 condensation reactivity is suppressed and selectivity of the reaction can be acquired, a hydrogen atom or an alkyl group having 1 to 5 carbon atoms can be preferably used.

Integer n in the formula determines the number of
10 condensation reactive silanol groups (in the case that R^2 is a hydrogen group) or the number of alkoxy groups (in the case that R^2 is an alkyl group having 1 to 5 carbon atoms) and is a large factor in determining the properties of polyorganosiloxane particles contained in the obtained an emulsion of polyorganosiloxane.

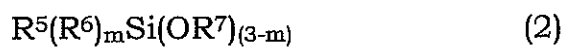
15 When $n=0$ or 1, because condensation reactive organosilane (I) has 4 or 3 condensation reactive groups and functions as a crosslinking agent of polyorganosiloxane (H), rubber elasticity can be imparted to the obtained polyorganosiloxane particles. On the other hand, when $n=2$, the condensation reactive organosilane is
20 difunctional condensation reactive organosilane and differs from the above case when $n=0$ or 1, as the condensation reactive organosilane does not function as a crosslinking agent and an emulsion of polyorganosiloxane containing particles of linear polyorganosiloxane can be obtained. The number of condensation reactive groups can be
25 selected according to the desired properties.

The amount of condensation reactive organosilane (I) that is added in the present invention is preferably 0.1 to 50 parts by weight,

more preferably 0.5 to 20 parts by weight based on 100 parts by weight of polyorganosiloxane (H). When the amount is too small, the effect of improving polymerization conversion ratio is not exhibited and when the amount is too large, problems may occur such as production of scale particles due to side reactions.

The alkoxysilane compound (J) in the present invention is an alkoxysilane compound having a radical-polymerizable functional group in a molecule and is a component necessary for obtaining the graft copolymer containing polyorganosiloxane described below.

The alkoxysilane compound (J) in the present invention is a compound having the structure shown in the following formula (2):



(wherein R^5 represents an organic group having a radical-polymerizable functional group, R^6 represents any organic group, which can be the same as R^5 , R^7 represents an alkyl group having 1 to 5 carbon atoms, m represents an integer of 0 or 1). Herein, radical-polymerizable functional group R^5 is not particularly limited, but a (meth)acryloyloxy group, a mercapto group, a vinyl group and a styryl group are preferable from the viewpoints of easily introducing functional groups and polymerization reactivity. As the alkoxysilane compound (J) component, more specific examples are silane compounds containing a (meth)acryloyloxy group such as γ -methacryloyloxypropyldimethoxymethylsilane, γ -methacryloyloxypropyltrimethoxysilane, γ -methacryloyloxypropyltriethoxysilane,

γ -methacryloyloxypropyldiethoxymethylsilane,
 γ -acryloyloxypropyldimethoxymethylsilane and
 γ -acryloyloxypropyltrimethoxysilane; silane compounds containing a
vinylphenyl group such as p-vinylphenyldimethoxymethylsilane and
5 p-vinylphenyltrimethoxysilane; silane compounds containing a vinyl
group such as vinylmethyldimethoxysilane, vinyltrimethoxysilane and
vinyltriethoxysilane and silane compounds containing a mercapto
group such as mercaptopropyltrimethoxysilane and
mercaptopropyldimethoxymethylsilane. Of these, silane compounds
10 containing a (meth)acryloyloxy group, silane compounds containing a
vinyl group and silane compounds containing a mercapto group are
preferably used from the viewpoint of economical efficiency.

Also, the alkoxysilane compound (J) wherein the number of
alkoxy groups OR⁷ bonded to a silicon atom is 2 (in the case that m=1
15 in formula 2) or 3 (in the case that m=0 in formula 2) is suitably used.
When the number of alkoxy groups is 2, the polyorganosiloxane
particles contained in the emulsion of polyorganosiloxane obtained by
the present invention has a linear structure and when the number of
alkoxy groups is 3, rubber elasticity can be imparted to the
20 polyorganosiloxane particles, since the alkoxysilane compound (J) has
function as a crosslinking agent.

The amount of alkoxysilane compound (J) is preferably 0.01
to 20 parts by weight, more preferably 0.1 to 10 parts by weight, based
on 100 parts by weight of cyclic organosiloxane. When the amount is
25 less than 0.01 part by weight, large agglomerate may develop when
coagulating and thermally treating and powder properties of the resin
may become poor. When the amount is more than 20 parts by weight,

impact resistance of the final molded article may decrease.

In the present invention, a primary emulsion is obtained by homogeneously emulsifying cyclic organosiloxane and when necessary, preferably 0.01 to 20 parts by weight of alkoxysilane compound having
5 a radical-polymerizable functional group in a molecule (J) based on 100 parts by weight of cyclic organosiloxane, together with a surfactant and water using an emulsifying instrument such as a homomixer, a colloid mill and a homogenizer and then emulsion polymerization is conducted. Herein, the amount of water that is used is not
10 particularly limited, as long as the amount is sufficient for emulsifying organosiloxane of a low polymerization degree. Usually, the amount of water is 10 to 500 parts by weight based on 100 parts by weight of cyclic organosiloxane. When the amount of water is less than 10 parts by weight, the amount of organosiloxane of a low polymerization
15 degree, which is hydrophobic oil, is too large and the emulsion does not invert from W/O to O/W. As a result, water has difficulty in becoming a continuous phase. When the amount is more than 500 parts by weight, stability tends to become poor. In emulsion polymerization, a surfactant that does not lose emulsifying ability
20 under acidic conditions is suitably used. Examples are alkylbenzene sulfonic acid, sodium alkylbenzene sulfonate, alkylsulfonic acid, sodium alkylsulfonate, sodium (di)alkyl sulfosuccinate, sodium polyoxyethylene nonylphenylether sulfonate and sodium alkyl sulfide. These may be used alone or two or more kinds can be used in
25 combination. Of these, alkylbenzene sulfonic acid, sodium alkylbenzene sulfonate, alkylsulfonic acid, sodium alkylsulfonate and sodium (di)alkyl sulfosuccinate are preferable from the viewpoint that

emulsion stability of the emulsion is relatively high. Furthermore, alkylbenzene sulfonic acid and alkylsulfonic acid also function as a polymerization catalyst of the polyorganoiloxane forming component and therefore are particularly preferable.

5 The amount of the surfactant that is used is preferably an amount of 0.05 to 20 % by weight, more preferably 0.1 to 10 % by weight, in the primary emulsion. When the amount of the surfactant is too small, stability of the obtained emulsion tends to decrease and on the other hand, when the amount is too large, applications of the
10 emulsion of polyorganosiloxane obtained by the present invention and the graft copolymer containing polyorganosiloxane obtained therefrom may be limited.

 In the primary emulsion, emulsion polymerization is conducted while stirring to obtain polyorganosiloxane (H). Emulsion
15 polymerization is preferably conducted under pH of at most 5 and the reaction temperature is preferably 30 to 95°C. When the temperature is lower than 30°C, the polymerization rate becomes slow and when the temperature is higher than 95°C, stability tends to become poor. When the polymerization time is less than 1 hour, polymerization is
20 insufficient and when polymerization is conducted for more than 100 hours, the polymerization reaction does not progress further. Therefore, polymerization is preferably 1 to 100 hours, more preferably 5 to 50 hours. The pH during emulsion polymerization is preferably at most 5. When the pH is more than 5, progression of polymerization
25 becomes slow and the conversion ratio tends to be unsatisfactory.

 Usually, under acidic conditions, Si-O-Si bonds, which form the structure of polyorganosiloxane obtained by polymerization of

cyclic organosiloxane, are in an equilibrium state of being decomposed and produced. Equilibrium changes according to the temperature and the lower the temperature is the easier the production of polyorganosiloxane having high molecular weight. Consequently, in polycondensation of polyorganosiloxane (H) and when necessary, alkoxy silane compound (J), in the present invention, heating is preferably stopped when the polymerization conversion ratio preferably reaches 75 % to 89 %, more preferably 82 to 89 %, cooling is preferably conducted to a temperature below the polymerization temperature, specifically preferably 10 to 50°C, more preferably 20 to 45°C, and then aging is preferably conducted for at least 6 hours. When the temperature is lower than 10°C, a long period of time is required for cooling and productivity is poor. When the temperature is higher than 50°C, molecular weight of polyorganosiloxane may not be made sufficiently high by aging. Usually, neutralization is conducted by an alkali component such as sodium hydroxide, potassium hydroxide and sodium carbonate in order to stabilize the polyorganosiloxane chains. However, in the present invention, because polyorganosiloxane is reacted with condensation reactive organosilane (I), neutralization by an alkali component such as sodium hydroxide, potassium hydroxide and sodium carbonate does not necessarily need to be conducted. However, when storing for a long period of time or controlling the molecular weight of polyorganosiloxane within a narrow range, neutralization can be conducted when necessary and then the polyorganosiloxane emulsion can be adjusted to acidic conditions to prepare the polyorganosiloxane emulsion of the present invention.

Subsequently, 0.01 to 20 part by weight of condensation

reactive organosilane (I) is added based on 100 parts by weight of the aged polyorganosiloxane (H). The temperature of the emulsion of polyorganosiloxane (H) when adding condensation reactive organosilane (I) is preferably 10 to 50°C, more preferably 20 to 45°C.

5 When the temperature is higher than 50°C, side reactions prevail before reaction with silanol groups of polyorganosiloxane in a micell and the effect of improving polymerization conversion ratio cannot be obtained. Furthermore, because by-products such as scale particles are produced by hydrolysis and condensation of condensation reactive
10 organosilane (I), properties of the emulsion of polyorganosiloxane and the graft copolymer containing polyorganosiloxane obtained therefrom may be adversely affected. Also, when the temperature is too low, a long period of time is required for cooling and reheating, thus being unfavorable in view of productivity.

15 The reaction temperature of condensation reactive organosilane (I) is preferably 30 to 95°C, more preferably 35 to 85°C. When the temperature is lower than 30°C, progression of the condensation reaction tends to be slow and the effect of improving conversion ratio tends to be insufficient. Also, condensation reactive
20 organosilane (I) is preferably reacted under pH of at most 5. When the pH is more than 5, progression of the condensation reaction tends to be slow and the effect of improving conversion ratio tends to be insufficient.

In the present invention, polymerization conversion ratio
25 refers to the conversion ratio of cyclic organosiloxane used when preparing polyorganosiloxane (H) to low volatile matter and is calculated from the solid content concentration when polymerizing.

More specifically, the polymerization conversion ratio is calculated from the equation:

Polymerization conversion ratio =

5
$$\frac{[(\text{parts by weight of all components in emulsion}) \times (\text{solid content concentration of polymerization emulsion}) - (\text{parts by weight of solid content other than cyclic organosiloxane})]}{(\text{parts by weight of cyclic organosiloxane})}$$

10 Herein, solid content concentration refers to the proportion of remnant solid content, when approximately 1 to 2 g of the emulsion when polymerizing is placed in an ointment can and then heated and dried for 1 hour in an oven of 130°C. In the present invention, by adding condensation reactive organosilane (I), the polymerization conversion
15 ratio of cyclic organosiloxane when preparing polyorganosiloxane (H) can be improved 5 to 10 %. Also, development of by-products such as scale particles can be inhibited. Furthermore, new functions can imparted by the functional groups contained in condensation reactive organosilane (I).

20 The graft copolymer containing polyorganosiloxane obtained from the emulsion of polyorganosiloxane of the present invention is described below.

The graft copolymer containing polyorganosiloxane obtained by the present invention is compounded in various thermoplastic
25 resins and thermosetting resins to provide a resin composition excellent in impact resistance.

The graft copolymer containing polyorganosiloxane of the

present invention is obtained by polymerizing, preferably 5 to 70 parts by weight, more preferably 10 to 50 parts by weight of a vinyl monomer, in the presence of preferably 95 to 30 parts by weight, more preferably 90 to 50 parts by weight of polyorganosiloxane particles contained in the emulsion of polyorganosiloxane obtained by the present invention, so that the total amount becomes 100 parts by weight. When the amount of polyorganosiloxane particles is too small, the effect of properties of the graft copolymer as a whole that are exhibited by polyorganosiloxane (such as impact absorbency, flame retardancy, water repellency) are not exhibited. When the amount of the vinyl monomer is too little, favorable dispersability in the matrix resin may not be obtained.

Examples of the vinyl monomer are aromatic alkenyl compounds such as styrene and α -methylstyrene; methacrylic esters such as methyl methacrylate, ethyl methacrylate, 2-ethylhexyl methacrylate and butyl methacrylate; acrylic esters such as methyl acrylate, ethyl acrylate and butyl acrylate; cyanized vinyl compounds such as acrylonitrile and methacrylonitrile; olefins such as ethylene and propylene; conjugated diolefins such as butadiene, isoprene and chloroprene; vinyl acetate; vinyl chloride; allyl methacrylate; triallyl isocyanurate and ethylene dimethacrylate. These may be used alone or two or more kinds can be used together.

For graft polymerization, normal seed emulsion polymerization can be employed and radical polymerization of the vinyl monomer can be conducted in the emulsion of polyorganosiloxane obtained by the present invention. The vinyl monomer can be polymerized in one step or two or more steps.

Radical polymerization can be conducted by the method of advancing reaction by thermally decomposing the radical polymerization initiator or by reacting in a redox system using a reducing agent and is not particularly limited.

5 As the radical polymerization initiator, the same radical polymerization initiators as those described above can be used. Also, as the reducing agent used in the redox system, the same reducing agents as those described above can be used.

10 The amount of the radical polymerization initiator that is used is preferably 0.005 to 20 parts by weight, more preferably 0.01 to 10 parts by weight, particularly preferably 0.03 to 5 parts by weight based on 100 parts by weight of the vinyl monomer that is used. When the amount of the radical polymerization initiator is less than 0.005 part by weight, the reaction rate is slow and production
15 efficiency tends to become poor. When the amount is more than 20 parts by weight, heat generation when reacting is large and preparation tends to become difficult.

20 Also, a chain transfer agent can be used when necessary in radical polymerization. The chain transfer can be any chain transfer agent that is usually used in emulsion polymerization and is not particularly limited.

 Examples of the chain transfer agent are t-dodecylmercaptan, n-octylmercaptan, n-tetradecylmercaptan and n-hexylmercaptan.

25 The chain transfer agent is an optional component but the amount when used is preferably 0.01 to 5 parts by weight based on 100 parts by weight of the vinyl monomer. When the amount of the

chain transfer agent is less than 0.01 part by weight, the effect of using the chain transfer agent cannot be obtained and when the amount is more than 5 parts by weight, the polymerization rate becomes slow and production efficiency tends to become low.

5 The reaction temperature when polymerizing is preferably 30 to 95°C.

 The graft copolymer containing polyorganosiloxane obtained by emulsion polymerization can be used by separating polymers from the emulsion or the emulsion can be used as it is. An example of the
10 method for separating the graft copolymer containing polyorganosiloxane is the method of coagulating by adding a metal salt such as calcium chloride, magnesium chloride and magnesium sulfate to the latex, separating, washing with water, dehydrating and drying the latex. Also, the spray drying method can be used.

15 Hereinafter, the present invention is described in detail by means of Examples but the present invention is not limited thereto. Measurement and tests in Examples and Comparative Examples were conducted in the following manner.

[Polymerization conversion ratio]

20 The amount of solid content of the latex was found by drying for 1 hour in a hot-air dryer of 120°C and then the polymerization conversion ratio was calculated from $100 \times \text{amount of solid content} / \text{amount of monomer (\%)}$.

[Volume average particle size]

25 The volume average particle size of the seed polymer, polyorganosiloxane particles and the graft copolymer were measured in a latex state. The volume average particle size (μm) was measured by

the light scattering method, using MICROTRAC UPA made by LEED & NORTHROP INSTRUMENTS as the measurement instrument.

[Impact resistance]

Impact resistance was evaluated according to ASTM D-256
5 by the Izod test at -10°C in Examples 1 to 6 and Comparative Example 1 and the Izod test at 0°C in Examples 13 to 18 and 24 to 28 and Comparative Examples 2 and 3 using a 1/8 inch bar having a notch.

[Flame retardancy]

Flame retardancy was evaluated by UL94 V test.

10 [Swellability]

With respect to latex of the seed polymer, particle size was measured by MICROTRAC UPA. A liquid obtained by mixing and emulsifying organosiloxane (octamethylcyclotetrasiloxane) in an amount of 50 times (by weight) of the seed polymer (solid content) and
15 the same amount of a 0.1 % by weight aqueous solution of Emar 2F (Kao Corporation) was mixed in 5 % by weight latex of the seed polymer. Then, the mixture was stirred for 1 hour at 23°C and the particle size was measured by MICROTRAC UPA.

The swelling volume ratio was measured from the following
20 equation.

Swelling volume ratio =

(particle size after swelling)/(particle size before swelling)³-1

25 [Tg]

The Tg of the seed polymer was found by differential thermal analysis (DTA).

EXAMPLES 1 to 3, 5 and 6

A five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with 300 parts by weight of deionized water and sodium dodecylbenzenesulfonate (SDBS) in the amount (solid content) shown in Table 1. After mixing, the temperature was raised to 50°C and when the temperature of the liquid reached 50°C, the inside of the flask was replaced with nitrogen. Then, 10 parts by weight of a mixed solution of butyl acrylate and styrene compounded in the ratio shown in Table 1 and 0.01 part by weight of para-menthane hydroperoxide was added. 30 minutes later, 0.002 part by weight of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.005 part by weight of disodium ethylenediaminetetraacetate and 0.2 part by weight of sodium formaldehyde sulfoxylate were added and polymerization was conducted further for 1 hour. Thereafter, a mixed solution containing 90 parts by weight of the mixed solution of butyl acrylate and styrene compounded in the ratio shown in Table 1 and 0.1 part by weight of para-menthane hydroperoxide was added continuously over 3 hours. 2 hours of post-polymerization was conducted and latex of a seed polymer (seed 1 to 5) was obtained. The volume average particle size and degree of swelling after synthesis was measured and the results are shown in Table 1.

A five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with 2 parts by weight of the seed polymer shown in Table 2. Then, a mixture comprising the components of 300

parts by weight of deionized water, 0.5 part by weight (solid content) of SDBS, 95 parts by weight of octamethylcyclotetrasiloxane and 5 parts by weight of mercaptopropyldimethoxymethylsilane (MPDS) was stirred for 5 minutes at 7000 rpm by a homomixer to prepare an emulsion and the emulsion was added all at once to the flask.

Then, 1 part by weight (solid content) of a 10 % aqueous solution of dodecylbenzenesulfonic acid was added and the temperature was raised to 80°C under nitrogen current while stirring. After stirring for 6 hours at 80°C, the mixture was cooled to 25°C and left for 20 hours. Thereafter, pH was adjusted to 6.5 by sodium hydroxide and polymerization was completed to obtain latex of polyorganosiloxane.

Subsequently, a five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with 240 parts by weight of deionized water and 70 parts by weight (solid content) of the above polyorganosiloxane particles and the temperature was raised to 40°C under nitrogen current while stirring. When the temperature reached 40°C, 0.2 part by weight of sodium formaldehyde sulfoxylate (SFS), 0.01 part by weight of disodium ethylenediaminetetraacetate (EDTA) and 0.0025 part by weight of ferrous sulfate were added. Then, a mixture of 3 parts by weight of allyl methacrylate (ALMA) and 0.01 part by weight (solid content) of cumene hydroperoxide was added all at once and stirring was continued for 1 hour at 40°C. Thereafter, a mixture of 30 parts by weight of methyl methacrylate (MMA) and 0.06 part by weight (solid content) of cumene hydroperoxide was added by dropping over 1.5 hours. After adding, stirring was continued for 1

hour to obtain latex of a graft copolymer. The volume average particle size is shown in Table 2.

Then, the latex was diluted with deionized water so that the solid content concentration becomes 15 % and then 4 parts by weight (solid content) of a 25 % aqueous solution of calcium chloride was added to obtain a coagulated slurry. After heating to 95°C, the coagulated slurry was cooled to 50°C, dehydrated and then dried to obtain powder of polyorganosiloxane graft copolymer.

Thereafter, polycarbonate resin (Tarflon® FN 1900A, available from Idemitsu Petrochemical Co., Ltd.) and the above powder of polyorganosiloxane graft copolymer were compounded in the composition shown in Table 2. The anti-dropping agent refers to polytetrafluoroethylene (Polyflon FA-500, available from Daikin Industries, Ltd.) and the stabilizer refers to a mixture of a phosphorous-type antioxidant (Adeka Stub PEP36, available from Asahi Denka Co., Ltd.) and a phenol-type antioxidant (Topanol CA, available from ICI Japan Co., Ltd.).

The obtained compound was melted and kneaded at 270°C by a twin-screw extruder (TEX 44SS, made by The Japan Steel Works, Ltd.) to prepare pellets. From the obtained pellets, specimen of 1/8 inch for evaluating impact resistance and specimen of 1/16 inch for evaluating flame retardancy were prepared using injection molding machine FAS 100B made by Fanuc Ltd. wherein the cylinder temperature was set to 280°C. Evaluation was conducted according to the evaluation methods described above using the obtained specimen. The results of impact resistance and flame retardancy of the molded article are shown in Table 2.

EXAMPLE 4

Synthesis, coagulation, thermal treatment, dehydration and drying to obtain powder, compounding, molding and evaluation were conducted in the same manner as in Example 1, except that the seed polymer was not added when polymerizing latex of polyorganosiloxane. The results are shown in Table 2.

COMPARATIVE EXAMPLE 1

Compounding, molding and evaluation were conducted in the same manner as in Example 1, except that the polyorganosiloxane graft copolymer was not added in the polycarbonate resin. The results are shown in Table 2.

15

TABLE 1

	Seed				
	1	2	3	4	5
Sodium dodecylbenzene sulfonate (phr)	24	16	16	6	6
Butyl acrylate (%)	100	100	80	100	0
Styrene (%)	0	0	20	0	100
Glass transition temperature (°C)	-45	-45	-15	105	-45
Average particle size (μm)	0.008	0.02	0.02	0.05	0.05
Swelling volume ratio (times)	20	15	12	1	0.5

TABLE 2

	Ex.						Com. Ex.
	1	2	3	4	5	6	
Composition							
Polycarbonate (part(s))	100	100	100	100	100	100	100
Anti-dropping agent (part(s))	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Stabilizer (part(s))	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Amount of flame retardant (part(s))	3	3	3	3	3	3	-
Flame retardant							
Seed polymer	Seed 1	Seed 2	Seed 3	-	Seed 4	Seed 5	-
Amount of seed (part(s))	2	2	2	-	2	2	-
Grafting agent	MPDS	MPDS	MPDS	MPDS	MPDS	MPDS	-
One-step graft	ALMA	ALMA	ALMA	ALMA	ALMA	ALMA	-
Second-step graft	MMA	MMA	MMA	MMA	MMA	MMA	-
Average particle size (μm)	0.23	0.23	0.25	0.2	0.2	0.2	-
Properties							
Impact resistance							
Izod Strength (kJ/m^2)	20	20	20	20	20	20	14
Flame retardancy							
Time for complete combustion (sec)	40	45	45	90	90	80	130
UL94V evaluation	V-0	V-0	V-0	V-2	V-2	V-2	Not-V

PREPARATION EXAMPLE 1

A five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with 300 parts by weight of deionized water and 8 parts by weight (solid content) of sodium dodecylbenzenesulfonate (SDBS). After mixing, the temperature was raised to 50°C and after the temperature of the liquid reached 50°C, the inside of the flask was replaced with nitrogen. Then, 10 parts by weight of butyl acrylate (BA), 3 parts by weight of t-dodecylmercaptan (tDM) and 0.01 part by weight of para-menthane hydroperoxide were added. 30 minutes later, 0.002 part by weight of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.005 part by weight of disodium ethylenediaminetetraacetate and 0.2 part by weight of sodium formaldehyde sulfoxylate were added and polymerization was conducted further for 1 hour. Thereafter, a mixed solution of 90 parts by weight of butyl acrylate, 27 parts by weight of t-dodecylmercaptan (tDM) and 0.1 part by weight of para-menthane hydroperoxide was added continuously over 3 hours. 2 hours of post-polymerization was conducted and latex of a seed polymer (SE-1) was obtained. The polymerization ratio of the obtained latex of the seed polymer was 92 % by weight and the volume average particle size was 0.04 μm .

PREPARATION EXAMPLE 2

A five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with 2 parts by weight (solid content) of the seed polymer of Preparation Example 1 (SE-1). Then, a mixture

comprising the components of 300 parts by weight of deionized water, 0.5 part by weight (solid content) of sodium dodecylbenzenesulfonate (SDBS), 98 parts by weight of octamethylcyclotetrasiloxane (D4) and 5 parts by weight of mercaptopropyltrimethoxymethylsilane (MPrDMS) was stirred for 5 minutes at 7000 rpm by a homomixer to prepare an emulsion and the emulsion was added all at once to the flask.

Then, 1 part by weight (solid content) of a 10 % aqueous solution of dodecylbenzenesulfonic acid was added and the temperature was raised to 80°C under nitrogen current while stirring. After stirring for 15 hours at 80°C, the mixture was cooled to 25°C and left for 30 hours. Thereafter, pH was adjusted to 6.5 by sodium hydroxide and polymerization was completed to obtain latex of polyorganosiloxane (SR-1). The polymerization ratio of the obtained latex of polyorganosiloxane was 85 % by weight and the volume average particle size was 0.28 μm .

EXAMPLES 7 to 12

A five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with 80 parts by weight (solid content) of the polyorganosiloxane particles obtained in Preparation Example 2 and the temperature was raised to 40°C under nitrogen current while stirring. When the temperature reached 40°C, 0.39 part by weight of sodium formaldehyde sulfoxylate (SFS), 0.004 part by weight of disodium ethylenediaminetetraacetate (EDTA) and 0.001 part by weight of ferrous sulfate were added. Then, 3 parts by weight of allyl methacrylate (ALMA) and RY-1 to 6 shown in Table 3 in the amounts

shown in Table 4 (2.11×10^{-4} mol) were mixed and then added all at once and stirring was continued for 1 hour at 40°C. Thereafter, 30 parts by weight of methyl methacrylate (MMA) and RY-1 to 6 shown in Table 3 in the amounts shown in Table 4 (4.21×10^{-4} mol) were mixed
5 and the mixture was added by dropping over 1.5 hours. After adding, stirring was continued for 3 hours to obtain latex of a graft copolymer. The polymerization ratio and volume average particle size of the obtained latex of a graft copolymer are shown in Table 4.

Subsequently, the latex was diluted with deionized water so
10 that the solid content concentration becomes 15 % and then 4 parts by weight (solid content) of a 2.5 % aqueous solution of calcium chloride was added to obtain a coagulated slurry. After heating to 95°C, the coagulated slurry was cooled to 50°C, dehydrated and then dried to obtain powder of polyorganosiloxane graft copolymer (SG-1 to 6).

15

EXAMPLES 13 to 18

Polycarbonate resin (product name: Panlite® L1225 WX, Teijin Chemicals, Ltd.), polytetrafluoroethylene (Polyflon FA-500, available from Daikin Industries, Ltd.) as the anti-dropping agent and
20 powder of polyorganosiloxane graft copolymer obtained in Examples 7 to 12 (SG-1 to 6) were compounded in the composition shown in Table 5.

The obtained compound was melted and kneaded at 270°C by a twin-screw extruder (TEX 44SS, made by The Japan Steel Works, Ltd.) to prepare pellets. From the obtained pellets, specimen of 1/20
25 inch for evaluating flame retardancy and specimen of 1/8 inch for evaluating impact resistance were prepared using injection molding

machine FAS 100B made by Fanuc Ltd. wherein the cylinder temperature was set to 280°C. Evaluation was conducted according to the evaluation methods described above using the obtained specimen. The results of impact resistance and flame retardancy of
5 the molded article are shown in Table 5.

COMPARATIVE EXAMPLE 2

Compounding, molding and evaluation were conducted in the same manner as in Example 13, except that the powder of
10 polyorganosiloxane graft copolymer was not added. The results are shown in Table 5.

TABLE 3

	Initiator No.	Solubility to water at 20°C (g/100g of water)	Hydrogen drawing properties MSD trapping method (%)	Molecular weight
t-hexyl hydroperoxide	RY-1	2	20	118
p-menthane hydroperoxide	RY-2	1.6	23	172
t-butyl hydroperoxide	RY-3	15.7	19	90
t-hexylperoxyisopropyl monocarbonate	RY-4	0.01	19	204
cumene hydroperoxide	RY-5	1.6	48	152
t-butylperoxyisopropyl monocarbonate	RY-6	0.02	47	176

TABLE 4

		Ex.					
		7	8	9	10	11	12
Polyorganosiloxane particles (A) (part(s))	SR-1	80	80	80	80	80	80
Vinyl monomer (B) (part(s))	ALMA	3	3	3	3	3	3
	RY	RY-1	RY-2	RY-3	RY-4	RY-5	RY-6
	2.11×10^{-4} mol	0.025	0.037	0.019	0.043	0.032	0.037
	MMA	20	20	20	20	20	20
Vinyl monomer (C) (part(s))	RY	RY-1	RY-2	RY-3	RY-4	RY-5	RY-6
	4.21×10^{-4} mol	0.05	0.072	0.038	0.086	0.064	0.074
Polymerization ratio (%)	Vinyl monomer (B) after reaction	99	99	99	99	99	99
	Vinyl monomer (C) after reaction	99	99	99	99	99	99
Particle size (μ m)		0.29	0.29	0.29	0.29	0.29	0.29
Graft copolymer No.		SG-1	SG-2	SG-3	SG-4	SG-5	SG-6

TABLE 5

	Ex.								Com. Ex.
	13	14	15	16	17	18	19	20	
Thermoplastic resin (part(s))	100	100	100	100	100	100	100	100	100
Graft copolymer (part(s))	SG-1	3	-	-	-	-	-	-	-
	SG-2	-	3	-	-	-	-	-	-
	SG-3	-	-	3	-	-	-	-	-
	SG-4	-	-	-	3	-	-	-	-
	SG-5	-	-	-	-	3	-	-	-
	SG-6	-	-	-	-	-	3	-	-
Anti-dropping agent (part(s))	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Polytetrafluoroethylene	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Flame retardancy of 1.2 mm thickness molded article	Time for complete combustion (sec)	40	45	92	61	62	52	90	
	Dripping	None	None	Yes	None	Yes	Yes	Yes	Yes
	Evaluation	V-0	V-0	V-2	V-1	V-1	V-1	Not-V	
Impact resistance 1/8 inc Izod Strength	24	24	24	24	20	24	24	14	

PREPARATION EXAMPLE 3

A five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with 2 parts by weight (solid content) of the seed polymer of Preparation Example 1 (SE-1). Then, a mixture comprising the components of 300 parts by weight of deionized water, 0.5 part by weight (solid content) of sodium dodecylbenzenesulfonate (SDBS), 98 parts by weight of octamethylcyclotetrasiloxane (D4) and 4 parts by weight of mercaptopropyldimethoxymethylsilane (MPrDMS) was stirred for 5 minutes at 7000 rpm by a homomixer to prepare an emulsion and the emulsion was added all at once to the flask.

Then, 1 part by weight (solid content) of a 10 % aqueous solution of dodecylbenzenesulfonic acid was added and the temperature was raised to 80°C under nitrogen current while stirring. After stirring for 15 hours at 80°C, the mixture was cooled to 25°C and left for 30 hours.

Subsequently, the temperature was raised to 40°C under nitrogen current while stirring the polyorganosiloxane particles. After the temperature reached 40°C, a mixture comprising the components of 5.2 parts by weight of deionized water, 1 part by weight of mercaptopropyldimethoxymethylsilane (MPrDMS) and 0.005 part by weight (solid content) of sodium dodecylbenzenesulfonate was stirred for 30 minutes with a stirrer to prepare an emulsion. The prepared emulsion was added all at once and stirring was continued for 5 minutes. Thereafter, 0.06 part by weight of sodium formaldehyde sulfoxylate (SFS), 0.0006 part by weight disodium ethylenediaminetetraacetate (EDTA) and 0.00015 part by weight of

ferrous sulfate were added and then a mixture of 3.8 parts by weight of allyl methacrylate (ALMA) and 0.1 part by weight (solid content) of t-butylperoxyisopropylcarbonate (RY-6) was added all at once. Stirring was continued for 3 hours at 40°C. Thereafter, pH was
5 adjusted to 6.5 by sodium hydroxide and polymerization was completed to obtain latex of polyorganosiloxane (SR-2). The polymerization ratio and the volume average particle size of the obtained latex of polyorganosiloxane are shown in Table 6.

10 PREPARATION EXAMPLE 4

Latex of polyorganosiloxane (SR-3) was obtained by synthesizing in the same manner as in Preparation Example 3, except that the amount of mercaptopropyldimethoxymethylsilane (MPrDMS) that is added at the same time as octamethylcyclotetrasiloxane (D4)
15 was 3 parts by weight and the components of the emulsion that is added after cooling, leaving and heating was 10.5 parts by weight of deionized water, 2 parts by weight of mercaptopropyldimethoxymethylsilane (MPrDMS) and 0.01 part by weight (solid content) sodium dodecylbenzenesulfonate (SDBS). The
20 polymerization ratio and the volume average particle size of the obtained latex of polyorganosiloxane are shown in Table 6.

PREPARATION EXAMPLE 5

Latex of polyorganosiloxane (SR-4) was obtained by
25 synthesizing in the same manner as in Preparation Example 3, except that the amount of mercaptopropyldimethoxymethylsilane (MPrDMS) that is added at the same time as octamethylcyclotetrasiloxane (D4)

was 2 parts by weight and the components of the emulsion that is added after cooling, leaving and heating was 15.7 parts by weight of deionized water, 3 parts by weight of mercaptopropyldimethoxymethylsilane (MPrDMS) and 0.015 part by weight (solid content) sodium dodecylbenzenesulfonate (SDBS). The polymerization ratio and the volume average particle size of the obtained latex of polyorganosiloxane are shown in Table 6.

PREPARATION EXAMPLE 6

Latex of polyorganosiloxane (SR-5) was obtained by synthesizing in the same manner as in Preparation Example 3, except that the amount of mercaptopropyldimethoxymethylsilane (MPrDMS) that is added at the same time as octamethylcyclotetrasiloxane (D4) was 5 parts by weight and the emulsion was not added after cooling, leaving and heating. The polymerization ratio and the volume average particle size of the obtained latex of polyorganosiloxane are shown in Table 6.

PREPARATION EXAMPLE 7

Latex of polyorganosiloxane (SR-6) was obtained by synthesizing in the same manner as in Preparation Example 3, except that the amount of mercaptopropyldimethoxymethylsilane (MPrDMS) that is added at the same time as octamethylcyclotetrasiloxane (D4) was 0 parts by weight and the components of the emulsion that is added after cooling, leaving and heating was 26.2 parts by weight of deionized water, 5 parts by weight of mercaptopropyldimethoxymethylsilane (MPrDMS) and 0.025 part by

weight (solid content) sodium dodecylbenzenesulfonate (SDBS). The polymerization ratio and the volume average particle size of the obtained latex of polyorganosiloxane are shown in Table 6.

5

EXAMPLES 19 to 23

A five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with 70 parts by weight (solid content) of polyorganosiloxane particles shown in Table 7 and the temperature
10 was raised to 40°C under nitrogen current while stirring. When the temperature reached 40°C, 0.39 part by weight of sodium formaldehyde sulfoxylate (SFS), 0.004 part by weight of disodium ethylenediaminetetraacetate (EDTA) and 0.001 part by weight of ferrous sulfate were added. Then, a mixture of 3 parts by weight of
15 allyl methacrylate (ALMA) and 0.11 part by weight (solid content) of p-menthane hydroperoxide (RY-2) was added all at once and stirring was continued for 1 hour at 40°C. Thereafter, a mixture of 30 parts by weight of methyl methacrylate (MMA) and 0.23 part by weight of p-menthanehydroperoxide (RY-2) was added by dropping over 1.5
20 hours. After adding, stirring was continued for 3 hours to obtain latex of a graft copolymer. The polymerization ratio and volume average particle size of the obtained latex of a graft copolymer are shown in Table 7.

Subsequently, the latex was diluted with deionized water so
25 that the solid content concentration becomes 15 % and then 4 parts by weight (solid content) of a 2.5 % aqueous solution of calcium chloride was added to obtain a coagulated slurry. After heating to 95°C, the

coagulated slurry was cooled to 50°C, dehydrated and then dried to obtain powder of polyorganosiloxane graft copolymer (SG-7 to 11).

EXAMPLES 24 to 28

5 Polycarbonate resin (product name: Panlite® L1225 WX, Teijin Chemicals, Ltd.), polytetrafluoroethylene (Polyflon FA-500, available from Daikin Industries, Ltd.) as the anti-dropping agent and powder of polyorganosiloxane graft copolymer obtained in Examples 19 to 23 (SG-7 to 11) were compounded in the composition shown in
10 Table 8.

The obtained compound was melted and kneaded at 270°C by a twin-screw extruder (TEX 44SS, made by The Japan Steel Works, Ltd.) to prepare pellets. From the obtained pellets, specimen of 1/20 inch for evaluating flame retardancy and specimen of 1/8 inch for
15 evaluating impact resistance were prepared using injection molding machine FAS 100B made by Fanuc Ltd. wherein the cylinder temperature was set to 280°C. Evaluation was conducted according to the evaluation methods described above using the obtained specimen. The results of impact resistance and flame retardancy of
20 the molded article are shown in Table 8.

COMPARATIVE EXAMPLE 3

Compounding, molding and evaluation were conducted in the same manner as in Example 24, except that the powder of
25 polyorganosiloxane graft copolymer was not added. The results are shown in Table 8.

TABLE 6

	Prep. Ex.						
	3	4	5	6	7		
Polyorganosiloxane (A) (part(s))							
SE-1	2	2	2	2	2	2	2
D4	98	98	98	98	98	98	98
MPtDMS	4	3	2	5	0	0	0
Grafting agent (F) (part(s))							
MPtDMS	1	2	3	0	5	5	5
Vinyl monomer (B) (part(s))							
ALMA	3.8	3.8	3.8	3.8	3.8	3.8	3.8
RY-6	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Polymerization ratio of monomer (%)							
Vinyl monomer (B) after reaction	99	99	99	99	99	99	99
Polymerization ratio of D4 (%)							
Polyorganosiloxane (A) after preparation	85	85	85	85	85	85	85
Vinyl monomer (B) after reaction	89	88	87.5	88.5	86.5	86.5	86.5
Particle size (μm)	0.23	0.24	0.24	0.23	0.25	0.25	0.25
Polyorganosiloxane particle No.	SR-2	SR-3	SR-4	SR-5	SR-6	SR-6	SR-6

TABLE 7

	Ex.					
	19	20	21	22	23	
Polyorganosiloxane (A) (part(s))	SR-2	70	-	-	-	-
	SR-3	-	70	-	-	-
	SR-4	-	-	70	-	-
	SR-5	-	-	-	70	-
	SR-6	-	-	-	-	70
	ALMA	3	3	3	3	3
Vinyl monomer (G) (part(s))	RY-2	0.11	0.11	0.11	0.11	0.11
Vinyl monomer (C) (part(s))	MMA	30	30	30	30	30
	RY-2	0.23	0.23	0.23	0.23	0.23
Polymerization ratio of octamethylcyclotetrasiloxane		91	91	88	90	87
Particle size (μm)		0.24	0.25	0.25	0.24	0.25
Graft copolymer No.		SG-7	SG-8	SG-9	SG-10	SG-11

TABLE 8

	Ex.					Com. Ex.	
	24	25	26	27	28	28	3
Thermoplastic resin (part(s))	100	100	100	100	100	100	100
	3	-	-	-	-	-	-
SG-7	3	-	-	-	-	-	-
SG-8	-	3	-	-	-	-	-
SG-9	-	-	3	-	-	-	-
SG-10	-	-	-	3	-	-	-
SG-11	-	-	-	-	3	-	-
Anti-dropping agent (part(s))	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	31	28	45	59	67	90	90
Flame retardancy of 1.2 mm thickness molded article	None	None	None	None	Yes	Yes	Yes
	V-0	V-0	V-0	V-1	Not-V	Not-V	Not-V
Impact resistance 1/8 inc Izod Strength	42	49	35	35	23	12	12

PREPARATION EXAMPLE 8

A mixture comprising 300 parts by weight of deionized water, 0.5 part by weight (solid content) of a 5 % aqueous solution of sodium dodecylbenzenesulfonate and 100 parts by weight of octamethylcyclotetrasiloxane was stirred for 5 minutes at 7000 rpm by a homomixer to prepare a primary emulsion of polyorganosiloxane. The emulsion was added all at once to a five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer.

Then, 1 part by weight (solid content) of a 10 % aqueous solution of dodecylbenzenesulfonic acid was added and the temperature was raised to 80°C under nitrogen current while stirring the system. When the temperature reached 80°C, stirring was continued for 6 hours at 80°C and then the mixture was cooled to 25°C and left for 20 hours. The polymerization conversion ratio of cyclic organosiloxane was 83 %. The pH of the emulsion was approximately 2.

PREPARATION EXAMPLE 9

A mixture comprising components of 300 parts by weight of deionized water, 0.5 part by weight (solid content) of a 5 % aqueous solution of sodium dodecylbenzenesulfonate, 100 parts by weight of octamethylcyclotetrasiloxane and 5 parts by weight of mercaptopropyltrimethoxymethylsilane was stirred for 5 minutes at 7000 rpm by a homomixer to prepare the primary emulsion of polyorganosiloxane. The emulsion was added all at once to a five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting

mouth, a monomer adding mouth and a thermometer.

Then, 1 part by weight (solid content) of a 10 % aqueous solution of dodecylbenzenesulfonic acid was added and the temperature was raised to 80°C under nitrogen current while stirring the system. When the temperature reached 80°C, stirring was continued for 6 hours at 80°C and then the mixture was cooled to 25°C and left for 20 hours. The polymerization conversion ratio of cyclic organosiloxane was 85 %. The pH of the emulsion was approximately 2.

10

EXAMPLE 29

To the emulsion of polyorganosiloxane obtained in Preparation Example 8, partially hydrolyzed condensate of tetramethoxysilane (product name: Methyl silicate 51, available from Tama Chemicals Co., Ltd.) was added in an amount equivalent to 5 parts by weight based on 100 parts by weight of the octamethylcyclotetrasiloxane that was used and reaction was conducted for 3 hours at 60°C. The pH when reacting was 2. After the reaction was finished, pH was adjusted to 6.9 by sodium hydrogen carbonate. The temperature of the emulsion of polyorganosiloxane when adding Methyl silicate 51 was 25°C.

1 g of the emulsion of polyorganosiloxane obtained in this way was placed in an ointment can and heated for 1 hour in an oven of 130°C. The solid content concentration was calculated and the polymerization conversion ratio was calculated therefrom. Evaluation of polymerization conversion ratio and scale amount are shown in Table 9.

EXAMPLE 30

To the emulsion of polyorganosiloxane obtained in
5 Preparation Example 8, tetraethoxysilane was added in an amount
equivalent to 5 parts by weight based on 100 parts by weight of the
octamethylcyclotetrasiloxane that was used and reacted for 3 hours at
80°C. The pH when reacting was 2. After the reaction was finished,
the pH was adjusted to 6.9 by sodium hydrogen carbonate. The
10 temperature of the emulsion of polyorganosiloxane when adding
tetraethoxysilane was 25°C.

1 g of the emulsion of polyorganosiloxane obtained in this
way was placed in an ointment can and heated for 1 hour in an oven of
130°C. The solid content concentration was calculated and the
15 polymerization conversion ratio was calculated therefrom. Evaluation
of polymerization conversion ratio and scale amount are shown in
Table 9.

EXAMPLE 31

20 To the emulsion of polyorganosiloxane obtained in
Preparation Example 8, diphenyldimethoxysilane was added in an
amount equivalent to 3 parts by weight based on 100 parts by weight
of the octamethylcyclotetrasiloxane that was used and reacted for 3
hours at 80°C. The pH when reacting was 2. After the reaction was
25 finished, the pH was adjusted to 6.9 by sodium hydrogen carbonate.
The temperature of the emulsion of polyorganosiloxane when adding
diphenyldimethoxysilane was 25°C. Evaluation of polymerization

conversion ratio and scale amount are shown in Table 9.

EXAMPLE 32

To the emulsion of polyorganosiloxane obtained in
5 Preparation Example 8, mercaptopropyltrimethoxysilane was added in
an amount equivalent to 5 parts by weight based on 100 parts by
weight of the octamethylcyclotetrasiloxane that was used and reacted
for 3 hours at 60°C. The pH when reacting was 2. After the reaction
was finished, the pH was adjusted to 6.9 by sodium hydrogen
10 carbonate. The temperature of the emulsion of polyorganosiloxane
when adding mercaptopropyltrimethoxysilane was 25°C.

1 g of the emulsion of polyorganosiloxane obtained in this
way was placed in an ointment can and heated for 1 hour in an oven of
130°C. The solid content concentration was calculated and the
15 polymerization conversion ratio was calculated therefrom. Evaluation
of polymerization conversion ratio and scale amount are shown in
Table 9.

EXAMPLE 33

20 To the emulsion of polyorganosiloxane obtained in
Preparation Example 9, partially hydrolyzed condensate of
tetramethoxysilane (product name: Methyl silicate 51, available from
Tama Chemicals Co., Ltd.) was added in an amount equivalent to 5
parts by weight based on 100 parts by weight of the
25 octamethylcyclotetrasiloxane that was used and reacted for 3 hours at
60°C. The pH when reacting was 2. After the reaction was finished,
the pH was adjusted to 6.9 by sodium hydrogen carbonate. The

temperature of the emulsion of polyorganosiloxane when adding Methyl silicate 51 was 25°C.

1 g of the emulsion of polyorganosiloxane obtained in this way was placed in an ointment can and heated for 1 hour in an oven of 130°C. The solid content concentration was calculated and the polymerization conversion ratio was calculated therefrom. Evaluation of polymerization conversion ratio and scale amount are shown in Table 9.

EXAMPLE 34

To the emulsion of polyorganosiloxane obtained in Preparation Example 9, tetraethoxysilane was added in an amount equivalent to 5 parts by weight based on 100 parts by weight of the octamethylcyclotetrasiloxane that was used and reacted for 3 hours at 80°C. The pH when reacting was 2. After the reaction was finished, the pH was adjusted to 6.9 by sodium hydrogen carbonate. The temperature of the emulsion of polyorganosiloxane when adding tetraethoxysilane was 25°C.

1 g of the emulsion of polyorganosiloxane obtained in this way was placed in an ointment can and heated for 1 hour in an oven of 130°C. The solid content concentration was calculated and the polymerization conversion ratio was calculated therefrom. Evaluation of polymerization conversion ratio and scale amount are shown in Table 9.

EXAMPLE 35

To the emulsion of polyorganosiloxane obtained in

Preparation Example 9, diphenyldimethoxysilane was added in an amount equivalent to 3 parts by weight based on 100 parts by weight of the octamethylcyclotetrasiloxane that was used and reacted for 3 hours at 80°C. The pH when reacting was 2. After the reaction was finished, the pH was adjusted to 6.9 by sodium hydrogen carbonate. The temperature of the emulsion of polyorganosiloxane when adding diphenylmethoxysilane was 25°C.

1 g of the emulsion of polyorganosiloxane obtained in this way was placed in an ointment can and heated for 1 hour in an oven of 130°C. The solid content concentration was calculated and the polymerization conversion ratio was calculated therefrom. Evaluation of polymerization conversion ratio and scale amount are shown in Table 9.

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EXAMPLE 36

To the emulsion of polyorganosiloxane obtained in Preparation Example 9, mercaptopropyltrimethoxysilane was added in an amount equivalent to 5 parts by weight based on 100 parts by weight of the octamethylcyclotetrasiloxane that was used and reacted for 3 hours at 60°C. The pH when reacting was 2. After the reaction was finished, the pH was adjusted to 6.9 by sodium hydrogen carbonate.

1 g of the emulsion of polyorganosiloxane obtained in this way was placed in an ointment can and heated for 1 hour in an oven of 130°C. The solid content concentration was calculated and the polymerization conversion ratio was calculated therefrom. Evaluation of polymerization conversion ratio and scale amount are shown in

Table 9.

COMPARATIVE EXAMPLE 4

5 A mixture comprising 300 parts by weight of deionized water, 0.5 part by weight (solid content) of a 5 % aqueous solution of sodium dodecylbenzenesulfonate, 100 parts by weight of octamethylcyclotetrasiloxane and 5 parts by weight of partially hydrolyzed condensate of tetramethoxysilane (product name: Methyl
10 silicate 51, available from Tama Chemicals Co., Ltd.) was stirred for 5 minutes at 7000 rpm by a homomixer to prepare a primary emulsion of polyorganosiloxane. The emulsion was added all at once to a five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer.

15 Then, 1 part by weight (solid content) of a 10 % aqueous solution of dodecylbenzenesulfonic acid was added and the temperature was raised to 80°C under nitrogen current while stirring the system. When the temperature reached 80°C, stirring was continued for 6 hours at 80°C and then the mixture was cooled to 25°C
20 and left for 20 hours. The mixture was neutralized by sodium hydrogen carbonate and the pH was adjusted to 6.8. The polymerization conversion ratio of cyclic organosiloxane was 87 %.

 1 g of the emulsion of polyorganosiloxane obtained in this way was placed in an ointment can and heated for 1 hour in an oven of
25 130°C. The solid content concentration was calculated and the polymerization conversion ratio was calculated therefrom. Evaluation of polymerization conversion ratio and scale amount are shown in

Table 9. A large number of scale particles developed on the bottom face, the side face and the stirring blades of the polymerization vessel.

TABLE 9

	Polymerization conversion ratio of emulsion before reaction with condensation reactive organosilane (I)	Polymerization conversion ratio of emulsion according to the present invention	Scale amount
Ex. 29	83	90	Small amount
Ex. 30	83	91	Small amount
Ex. 31	83	92	None
Ex. 32	83	89	Small amount
Ex. 33	85	91	Small amount
Ex. 34	85	92	Small amount
Ex. 35	85	92	None
Ex. 36	85	89	Small amount
Com. Ex. 4	87	-	Large amount

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The above results clearly indicate that according to the present invention, polymerization conversion ratio can be improved and development of scale particles can be inhibited.

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EXAMPLE 37

A five-neck flask equipped with a stirrer, a reflux condenser, a nitrogen injecting mouth, a monomer adding mouth and a thermometer was charged with the emulsion of polyorganosiloxane obtained in Example 30 in an amount of 70 parts by weight (solid content) of polyorganosiloxane particles and 240 parts by weight of

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deionized water (including water contained in the emulsion of polyorganosiloxane). The temperature was raised to 40°C under nitrogen current while stirring the system. When the temperature reached 40°C, 0.2 part by weight of sodium formaldehyde sulfoxylate (SFS), 0.01 part by weight of disodium ethylenediaminetetraacetate (EDTA) and 0.0025 part by weight of ferrous sulfate were added. Then, a mixture of 1 part by weight of allyl methacrylate (ALMA) and 0.01 part by weight (solid content) of cumene hydroperoxide was added all at once and stirring was continued for 1 hour at 40°C. Thereafter, a mixture of 30 parts by weight of methyl methacrylate and 0.06 part by weight of cumene hydroperoxide was added by dropping over 1.5 hours. After adding, stirring was continued further for 1 hour to obtain latex of a graft copolymer. The polymerization conversion ratio of the vinyl monomer was 99 %.

Subsequently, the latex was diluted with deionized water so that the solid content becomes 15 % and then 4 parts by weight (solid content) of a 25 % aqueous solution of calcium chloride was added to obtain a coagulated slurry. After heating to 85°C, the coagulated slurry was cooled to 50°C, dehydrated and then dried to obtain powder of polyorganosiloxane graft copolymer. Appearance of the obtained powder was favorable.

INDUSTRIAL APPLICABILITY

According to the present invention, a flame retardant can be obtained, which provides a thermoplastic resin composition excellent in flame retardancy and impact resistance, and by compounding this flame retardant in thermoplastic resin, a flame retardant resin

composition excellent in flame retardancy and impact resistance can be obtained.

Also, according to the present invention, in a process for preparing an emulsion of polyorganosiloxane, polymerization
5 conversion ratio can be improved.

CLAIMS

1. A graft copolymer containing polyorganosiloxane obtained by polymerizing,
5 0 to 10 parts by weight of a vinyl monomer (B) comprising 100 to 20 % by weight of a multi-functional monomer containing at least two polymerizable unsaturated bonds in a molecule (b-1) and 0 to 80 % by weight of another copolymerizable monomer (b-2) and
10 5 to 70 parts by weight of a vinyl monomer (C),
in the presence of 30 to 95 parts by weight of polyorganosiloxane in a latex state (A),
so that the total amount of polyorganosiloxane (A), vinyl monomer (B) and vinyl monomer (C) becomes 100 parts by weight.
- 15 2. The graft copolymer containing polyorganosiloxane of Claim 1, wherein polyorganosiloxane (A) is obtained by seed polymerizing organosiloxane using a seed polymer that is swelled by organosiloxane.
- 20 3. The graft copolymer containing polyorganosiloxane of Claim 2, wherein the particle size of said seed polymer is 0.001 to 0.03 μm .
- 25 4. The graft copolymer containing polyorganosiloxane of Claim 2, wherein Tg of said seed polymer is at most 0°C.
5. The graft copolymer containing polyorganosiloxane of

Claim 2, wherein the proportion of said seed polymer to polyorganosiloxane (A) is 0.1 to 10 % by weight.

6. The graft copolymer containing polyorganosiloxane of
5 Claim 2, wherein the swelling volume ratio of said seed polymer is 3 to 50 times.

7. The graft copolymer containing polyorganosiloxane of
10 Claim 2, wherein the swelling volume ratio of said seed polymer is 5 to 25 times.

8. The graft copolymer containing polyorganosiloxane of
Claim 1, wherein vinyl monomer (C) is at least one monomer selected
from the group consisting of an aromatic vinyl monomer, a cyanized
15 vinyl monomer, a (meth)acrylic ester monomer and a vinyl monomer
containing a carboxyl group.

9. The graft copolymer containing polyorganosiloxane of
Claim 1, wherein a radical polymerization initiator (D) having solubility
20 to water of 0.5 to 10 g/100 g (20°C) and hydrogen drawing properties
of 10 to 30 % is used when polymerizing vinyl monomer (B) and/or
vinyl monomer (C).

10. The graft copolymer containing polyorganosiloxane of
25 Claim 1, wherein polyorganosiloxane (A) is modified by a grafting agent
(E).

11. The graft copolymer containing polyorganosiloxane of Claim 10, wherein the amount of grafting agent (E) is 0.1 to 10 parts by weight based on 100 parts by weight of polyorganosiloxane (A).

5 12. The graft copolymer containing polyorganosiloxane of Claim 10, obtained by reacting polyorganosiloxane (A), which is modified by grafting agent (E), with grafting agent (F) and then polymerizing vinyl monomer (B) and vinyl monomer (C).

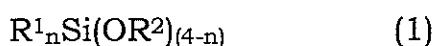
10 13. The graft copolymer containing polyorganosiloxane of Claim 12, wherein the reaction temperature of grafting agent (F) and vinyl monomer (B) is 20 to 60°C.

15 14. A flame retardant comprising the graft copolymer containing polyorganosiloxane of Claim 1.

15. A resin composition comprising 0.1 to 20 parts by weight of the flame retardant of Claim 14 based on 100 parts by weight of thermoplastic resin.

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16. A process for preparing an emulsion of polyorganosiloxane which comprises obtaining polyorganosiloxane (H) by emulsion polymerizing cyclic organosiloxane under acidic conditions of pH of at most 5; and
25 adding condensation reactive organosilane represented by formula (1):



(wherein R^1 represents an organic group, R^2 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, n represents an integer of 0 to 3)
or a partially hydrolyzed condensate thereof (I).

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17. The process for preparing an emulsion of polyorganosiloxane of Claim 16, wherein 0.1 to 50 parts by weight of condensation reactive organosilane or partially hydrolyzed condensate thereof (I) is added based on 100 parts by weight of polyorganosiloxane
10 (H) and reaction is conducted at a temperature of 30 to 95°C under acidic conditions of pH of at most 5.

18. The process for preparing an emulsion of polyorganosiloxane of Claim 17, wherein the temperature of
15 polyorganosiloxane (H) when adding condensation reactive organosilane or partially hydrolyzed condensate thereof (I) is 10 to 50°C.

19. The process for preparing an emulsion of
20 polyorganosiloxane of Claim 16, wherein polyorganosiloxane (H) is obtained by polymerizing 100 parts by weight of cyclic organosiloxane and 0.01 to 20 parts by weight an alkoxysilane compound having a radical-polymerizable functional group in a molecule (J).

25 20. The process for preparing an emulsion of polyorganosiloxane of Claim 16, wherein polyorganosiloxane (H) is obtained by emulsion polymerizing under acidic conditions and then

aging at a temperature of 10 to 50°C for at least 6 hours.

21. The process for preparing an emulsion of polyorganosiloxane of Claim 19, wherein said radical-polymerizable functional group of alkoxysilane compound (J) is at least one
5 functional group selected from the group consisting of a (meth)acryloyloxy group, a mercapto group, a vinyl group and a styryl group.

22. A graft copolymer containing polyorganosiloxane
10 obtained by polymerizing 5 to 70 parts by weight of a vinyl monomer based on 95 to 30 parts by weight of polyorganosiloxane particles in the emulsion of polyorganosiloxane obtained by the process of Claim 16, so that the total amount becomes 100 parts by weight.