

DESCRIPTION

PRODUCTION OF ACRYLIC RUBBER AND OBTAINED ACRYLIC RUBBER

TECHNICAL FIELD

[0001] The present invention relates to a method for producing an acrylic rubber, and more particularly, to a method for producing an acrylic rubber, the method being capable of preventing generation of mutual adhesion between hydrous crumbs and providing a high polymer recovery ratio, and the acrylic rubber being excellent in drying property and roll processability and being able to provide a cross-linked rubber that has excellent water resistance.

BACKGROUND ART

[0002] Acrylic rubber is a group of polymers comprising an acrylic acid ester as a main component, and is commonly recognized as a rubber having heat resistance, oil resistance, and ozone resistance, and is widely used in automobile-related fields.

[0003] Such acrylic rubber is usually produced by emulsion polymerizing a monomer mixture constituting the acrylic rubber; adding a coagulant to the obtained polymerized emulsion liquid to cause coagulation; and drying hydrous crumbs obtained by the coagulation (for example, see Patent Document 1).

[0004] For example, Patent Document 1 discloses a method for producing an acrylic rubber by adding a polymerized emulsion liquid obtained by emulsion polymerizing a monomer containing a cross-linkable monomer such as (meth)acrylate and butenoic monobutyrates in the presence of sodium dodecyl sulfate as an anionic emulsifier and a polyoxyethylene dodecyl ether as a nonionic emulsifier with using a polymerization catalyst composed of cumene hydroperoxide, ferrous sulfate, and sodium

formaldehyde sulfoxylate into 15 % saline at 80 °C to coagulate thereby obtaining a crumb; washing the crumb with water; and drying the washed one.

[0005] However, in the conventional acrylic rubber such as the acrylic rubber described in Patent Document 1, mutual adhesion between hydrous crumbs after coagulation may occur. When such mutual adhesion between the hydrous crumbs occurs, there has been a problem that the efficiency of washing after the coagulation is lowered, a drying time when drying the hydrous crumbs is required to be prolonged, a polymer recovery ratio is deteriorated, and the like, and thus productivity is lowered. In addition, there has been a problem that sticking to a roll when various compounding agents are blended using a roll tends to occur, and thus processability when performing a processing with a roll is not sufficient, and also a problem that water resistance is greatly decreased.

RELATED ART DOCUMENTS

PATENT DOCUMENTS

[0006] Patent Document 1: Japanese Unexamined Patent Application Publication No. 2011-88956

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0007] The present invention has been accomplished in view of such circumstances. The present invention aims to provide a method for producing an acrylic rubber, the method being able to effectively prevent generation of the mutual adhesion between hydrous crumbs and providing a high polymer recovery ratio, and the acrylic rubber being excellent in drying property and roll processability and being capable of providing a cross-linked rubber that has excellent water resistance.

MEANS FOR SOLVING THE PROBLEM

[0008] As a result of extensive studies to achieve the above object, the present inventors have found that the above object can be achieved by coagulating a polymerized emulsion liquid in the presence of two or more types of compounds having a polyoxyalkylene skeleton when the polymerized emulsion liquid obtained by emulsion polymerizing a monomer for forming an acrylic rubber is coagulated.

[0009] In addition, the present inventors have further found that the effectiveness of the present invention is greatly improved by using a particular catalyst or a particular coagulant, and a particular coagulation temperature, as well as by performing acid washing in the washing step.

The present inventors have completed the present invention based on these findings.

[0010] Accordingly, the present invention provides a method for producing an acrylic rubber, comprising: an emulsion polymerization step of emulsion polymerizing a monomer for forming the acrylic rubber so as to obtain a polymerized emulsion liquid; and a coagulation step of coagulating the polymerized emulsion liquid in the presence of two or more types of compounds having a polyoxyalkylene skeleton so as to obtain a hydrous crumb.

According to the method for producing the acrylic rubber of the present invention, it is preferable that the coagulation step is a step of obtaining the hydrous crumb by coagulating the polymerized emulsion liquid in the presence of two or more types of compounds having the polyoxyalkylene skeleton, the compounds having different molecular weights.

According to the method for producing the acrylic rubber of the present invention, it is preferable that the coagulating step is a

step of obtaining the hydrous crumb by coagulating the polymerized emulsion liquid in the presence of a polyalkylene glycol (A) and an ester compound of a polyalkylene glycol (B1) and/or an ether compound of a polyalkylene glycol (B2).

[0011] According to the method for producing the acrylic rubber of the present invention, it is preferable that emulsion polymerization in the emulsion polymerization step is performed with using a material containing a peroxide, ferrous sulfate, and an ascorbic acid or a salt of an ascorbic acid as a polymerization catalyst.

According to the method for producing the acrylic rubber of the present invention, it is preferable that coagulation in the coagulation step is performed by contacting the polymerized emulsion liquid with a sulfate compound.

According to the method for producing the acrylic rubber of the present invention, it is preferable that a coagulation temperature in the coagulation step is 60 °C or more.

According to the method for producing the acrylic rubber of the present invention, it is preferable that the method comprises: a washing step of performing washing on the hydrous crumb; and a drying step of drying the washed hydrous crumb, and it is preferable that the washing step comprises an acid washing.

[0012] Further, the present invention provides an acrylic rubber obtained by the above-mentioned methods.

In addition, the present invention provides a rubber composition comprising a rubber ingredient and a cross-linking agent, the rubber ingredient comprising the above-mentioned acrylic rubber; and a cross-linked rubber prepared by cross-linking such a rubber composition.

EFFECTS OF INVENTION

[0013] According to the present invention, there is provided a method for producing an acrylic rubber, the method being able to effectively prevent generation of the mutual adhesion between hydrous crumbs and providing a high polymer recovery ratio, and the acrylic rubber being excellent in drying property and roll processability and being capable of providing a cross-linked rubber that has excellent water resistance.

DESCRIPTION OF EMBODIMENTS

[0014] [Production method]

A method for producing an acrylic rubber of the present invention comprises: an emulsion polymerization step of emulsion polymerizing a monomer for forming an acrylic rubber so as to obtain a polymerized emulsion liquid; and

a coagulation step of coagulating the polymerized emulsion liquid in the presence of two or more types of compounds having a polyoxyalkylene skeleton so as to obtain a hydrous crumb.

[0015] <Monomer>

The monomer used in the present invention is characterized in that a (meth)acrylic ester is a main component. Note that, the (meth)acrylic ester indicates an acrylic ester and/or a methacrylic ester, and hereinafter, the same is true of (meth)acrylic acid methyl and the like. Further, the main component means a component having preferably 30 wt% or more in the total rubber monomer units. As the (meth)acrylic ester which is a main component, there is no particular limitation, and examples thereof include (meth)acrylic acid alkyl esters and (meth)acrylic acid alkoxyalkyl esters.

[0016] As the (meth)acrylic acid alkyl ester, for example, an ester of an alkanol having 1 to 12 carbon atoms and a (meth)acrylic acid is used, and an ester of an alkanol having 1 to 8 carbon atoms and a

(meth)acrylic acid is preferred, and an alkanol having 2 to 6 carbon atoms and an ester of a (meth)acrylic acid is more preferred. Specific examples thereof include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate. Among these, ethyl (meth)acrylate and n-butyl (meth)acrylate are preferred, and ethyl acrylate and n-butyl acrylate are particularly preferred.

[0017] As the (meth)acrylic acid alkoxyalkyl ester, for example, an ester of an alkoxyalkyl alcohol having 2 to 12 carbon atoms and a (meth)acrylic acid is preferred, and specifically examples thereof include methoxymethyl (meth)acrylate, ethoxymethyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-propoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 3-methoxypropyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, and the like. Among these, 2-ethoxyethyl (meth)acrylate and 2-methoxyethyl (meth)acrylate are preferable, and 2-ethoxyethyl acrylate and 2-methoxyethyl acrylate are more preferable.

[0018] Each of these (meth)acrylic acid esters may be used alone or in combination of two or more thereof. The content of the (meth)acrylic acid ester in the monomer is usually in the range of 50 to 99.9 wt%, preferably in the range of 60 to 99.7 wt%, and more preferably in the range of 70 to 99.5 wt%. When the content of the (meth)acrylic acid ester is excessively small, the weather resistance, heat resistance, and oil resistance of the obtained cross-linked rubber may decrease, and on the other hand, when it is excessively large, heat resistance of the obtained cross-linked rubber may decrease. Further, as the (meth)acrylic acid ester, those composed of (meth)acrylic acid alkyl ester in the range of 30 to 100 wt% and (meth)acrylic acid alkoxyalkyl ester in the range of 70 to 0 wt% are preferably used.

[0019] As a monomer in the emulsion polymerization step of the present invention, since the effect of the present invention improves largely, a monomer is suitable in which a cross-linkable monomer together with the above-mentioned (meth)acrylic acid ester are contained.

As the cross-linkable monomer, there is no particular limitation, and examples thereof include a carboxyl group-containing monomer, an epoxy group-containing monomer, a halogen atom-containing monomer, a diene monomer, and the like, and preferably a carboxyl group-containing monomer, an epoxy group-containing monomer, and a halogen atom-containing monomer, and more preferably a carboxyl group-containing monomer. It is suitable to comprise the carboxyl group-containing monomer since compression set resistance property of a cross-linked acrylic rubber highly improves.

[0020] As the carboxyl group-containing monomer, there is no particular limitation, but suitably, an α,β -ethylenically unsaturated carboxylic acid can be suitably used. Examples of the α,β -ethylenically unsaturated carboxylic acid include an α,β -ethylenically unsaturated monocarboxylic acid having 3 to 12 carbon atoms, an α,β -ethylenically unsaturated dicarboxylic acid having 4 to 12 carbon atoms, and a monoester of an α,β -ethylenically unsaturated dicarboxylic acids having 4 to 12 carbon atoms and an alkanol having 1 to 8 carbon atoms. By using an α,β -ethylenically unsaturated carboxylic acid, it is preferable to further enhance compression set resistance when the obtained acrylic rubber is cross-linked to form a cross-linked rubber.

[0021] Examples of the α,β -ethylenically unsaturated monocarboxylic acids having 3 to 12 carbon atoms include acrylic acid, methacrylic acid, α -ethylacrylic acid, crotonic acid, cinnamic acid, and the like. Examples of the α,β -ethylenically unsaturated dicarboxylic acids having 4 to 12 carbon atoms include butenedioic acids such as fumaric acid and

maleic acid, itaconic acid, citraconic acid, chloromaleic acid, and the like. Examples of monoesters of the α,β -ethylenically unsaturated dicarboxylic acid having 4 to 12 carbon atoms and alkanols having 1 to 8 carbon atoms include linear mono-alkyl esters of butenedioic acid such as monomethyl fumarate, monoethyl fumarate, mono-n-butyl fumarate, monomethyl maleate, monoethyl maleate, and mono-n-butyl maleate; butenedioic acid monoesters having an alicyclic structure such as monocyclopentyl fumarate, monocyclohexyl fumarate, monocyclohexenyl fumarate, monocyclopentyl maleate, monocyclohexyl maleate, and monocyclohexenyl maleate; itaconic acid monoesters such as monomethyl itaconate, monoethyl itaconate, mono-n-butyl itaconate, and monocyclohexyl itaconate; and the like.

[0022] As the carboxyl group-containing monomer, an α,β -ethylenically unsaturated carboxylic acid is preferred, a monoester of an α,β -ethylenically unsaturated dicarboxylic acid having 4 to 12 carbon atoms and an alcohol having 1 to 8 carbon atoms is more preferred, and a butenedionic acid mono-linear alkyl ester and a butenedionic acid monoester having an alicyclic structure are particularly preferred. Preferred specific examples thereof include mono-n-butyl fumarate, mono-n-butyl maleate, monocyclohexyl fumarate, monocyclohexyl maleate, and the like, and mono-n-butyl fumarate is particularly preferred. Among these monomers listed above, the dicarboxylic acids include those present as anhydrides thereof.

[0023] Examples of the epoxy group-containing monomer include, but are not limited to, an epoxy group-containing (meth)acrylic acid ester such as glycidyl (meth)acrylate; allyl glycidyl ether, vinyl glycidyl ether, and the like.

[0024] Any halogen atom-containing monomer can be used without a particular limitation. Examples thereof include unsaturated alcohol esters of halogen-containing saturated carboxylic acids, haloalkyl

(meth)acrylates, haloacyloxyalkyl (meth)acrylates, (haloacetylcarbamoyloxy)alkyl (meth)acrylates, halogen-containing unsaturated ethers, halogen-containing unsaturated ketones, halomethyl group-containing aromatic vinyl compounds, halogen-containing unsaturated amides, haloacetyl group-containing unsaturated monomers, and the like.

[0025] Examples of the unsaturated alcohol esters of halogen-containing saturated carboxylic acids include vinyl chloroacetate, vinyl 2-chloropropionate, allyl chloroacetate, and the like. Examples of the haloalkyl (meth)acrylates include chloromethyl (meth)acrylate, 1-chloroethyl (meth)acrylate, 2-chloroethyl (meth)acrylate, 1,2-dichloroethyl (meth)acrylate, 2-chloropropyl (meth)acrylate, 3-chloropropyl (meth)acrylate, 2,3-dichloropropyl (meth)acrylate, and the like. Examples of the haloacyloxyalkyl (meth)acrylates include 2-(chloroacetoxy)ethyl (meth)acrylate, 2-(chloroacetoxy)propyl (meth)acrylate, 3-(chloroacetoxy)propyl (meth)acrylate, 3-(hydroxychloroacetoxy)propyl (meth)acrylate, and the like. Examples of the (haloacetylcarbamoyloxy)alkyl (meth)acrylates include 2-(chloroacetylcarbamoyloxy)ethyl (meth)acrylate, 3-(chloroacetylcarbamoyloxy)propyl (meth)acrylate, and the like. Examples of the halogen-containing unsaturated ethers include chloromethylvinyl ether, 2-chloroethylvinyl ether, 3-chloropropylvinyl ether, 2-chloroethylallyl ether, 3-chloropropylallyl ether, and the like. Examples of the halogen-containing unsaturated ketones include 2-chloroethylvinyl ketone, 3-chloropropylvinyl ketone, 2-chloroethylallyl ketone, and the like. Examples of the halomethyl group-containing aromatic vinyl compounds include p-chloromethylstyrene, m-chloromethylstyrene, o-chloromethylstyrene, p-chloromethyl- α -methylstyrene, and the like. Examples of the halogen-containing unsaturated amides include N-chloromethyl(meth)acrylamide, and the like.

Examples of the haloacetyl group-containing unsaturated monomers include 3-(hydroxychloroacetoxy)propyl allyl ether, p-vinylbenzyl chloroacetate, and the like.

[0026] Examples of the diene monomers include conjugated dienes and non-conjugated dienes. Examples of the conjugated diene include 1,3-butadiene, isoprene, piperylene, and the like. Examples of the non-conjugated diene include ethylidene norbornene, dicyclopentadiene, dicyclopentadienyl (meth)acrylate, 2-dicyclopentadienylethyl (meth)acrylate, and the like.

[0027] These cross-linkable monomers may be used alone or in combination of two or more thereof. The content of the cross-linkable monomer in the monomer is usually in the range of 0.01 to 20 wt%, preferably in the range of 0.1 to 10 wt%, and more preferably in the range of 0.5 to 5 wt%. By setting the content of the cross-linkable monomer within the above range, stains of the polymerization tank does not occur when producing the acrylic rubber, and the rubber recovery ratio is also high, and further, it is possible to highly improve the water resistance and compression set resistance when the acrylic rubber is made into a cross-linked product, which is suitable.

[0028] The monomer used in the present invention may include other copolymerizable monomers as required in addition to the above-mentioned (meth)acrylic acid ester and cross-linkable monomer. The other copolymerizable monomers include, but are not limited to, an aromatic vinyl monomer, an α,β -ethylenically unsaturated nitrile monomer, an acrylamide monomer, other olefinic monomers, and the like, as long as they are copolymerizable. Examples of the aromatic vinyl monomer include styrene, α -methylstyrene, divinylbenzene, and the like. Examples of the α,β -ethylenically unsaturated nitrile monomer include acrylonitrile, methacrylonitrile, and the like. Examples of the acrylamide monomer include acrylamide, methacrylamide, and the like. Examples of the other

olefin monomers include ethylene, propylene, vinyl chloride, vinylidene chloride, vinyl acetate, ethyl vinyl ether, butyl vinyl ether, and the like. Among these additional copolymerizable monomers, styrene, acrylonitrile, methacrylonitrile, ethylene, and vinyl acetate are preferred, and acrylonitrile, methacrylonitrile, and ethylene are more preferred.

[0029] These other copolymerizable monomers may be used alone or in combination of two or more thereof. The content of these other copolymerizable monomers in the monomer is usually 49.99 wt% or less, preferably 39.9 wt% or less, and more preferably 29.5 wt% or less.

[0030] <Emulsion polymerization step>

The emulsion polymerization step in the production method of the present invention is characterized in that a monomer for forming the acrylic rubber described above is emulsion polymerized with using a polymerization catalyst to obtain a polymerized emulsion liquid.

As the emulsion polymerization method, a conventional method may be applied, and for example, a monomer for forming an acrylic rubber described above is mixed with an emulsifier and water in advance to prepare a monomer emulsion, and then a polymerization initiator is added to perform the emulsion polymerization.

[0031] The emulsifier includes, but are not limited to, a nonionic emulsifier, an anionic emulsifier, a cationic emulsifier, and the like.

The nonionic emulsifier is not particularly limited, and may include, for example, a polyoxyalkylene fatty acid ester such as polyoxyethylene stearic acid ester and polyoxyethylene sorbitan alkyl ester; a polyoxyalkylene alkyl ether such as polyoxyethylene dodecyl ether; a polyoxyalkylene alkyl phenyl ether such as polyoxyethylene nonyl phenyl ether; and the like, and a polyoxyalkylene alkyl ether and a polyoxyalkylene alkyl phenyl ether are preferable, and a polyoxyethylene alkyl ether and a polyoxyethylene alkyl phenyl ether are

more preferable. The production method of the present invention comprises the coagulation step of obtaining a hydrous crumb by coagulating a polymerized emulsion liquid, which is obtained in the emulsion polymerization step in the presence of two or more types of compounds having a polyoxyalkylene skeleton after the emulsion polymerization step. In the production method of the present invention, the nonionic emulsifier exemplified above acts as a emulsifier and also corresponds to the compounds having the polyoxyalkylene skeleton described above. In other words, as a nonionic emulsifier, by containing these compounds, they can remain in the polymerized emulsion liquid obtained by polymerization, and therefore, even at the time of coagulation, it is possible to perform a coagulation operation while the compounds being present as it is as a compound constituting two or more types of compounds having a polyoxyalkylene skeleton.

[0032] The weight average molecular weight (Mw) of the nonionic emulsifier is usually less than 10,000, but is preferably in the range of 100 to 8,000, more preferably 200 to 5,000, and most preferably 300 to 3,000, and the nonionic emulsifier having such a polyoxyalkylene skeleton corresponds to a low molecular weight compound ($\alpha 1$) having a weight average molecular weight (Mw) of less than 10,000, which is described later.

[0033] There is no particular limitation for the anionic emulsifier, and examples thereof include a salt of a fatty acid such as myristic acid, palmitic acid, oleic acid, linolenic acid; alkylbenzenesulfonates such as sodium dodecylbenzenesulfonate; a sulfate ester salt such as sodium lauryl sulfate, preferably a higher alcohol sulfate ester salt such as sodium sulfate ester of an alcohol having 6 or more carbon atoms; a phosphate ester salt such as sodium alkyl phosphate ester, preferably a higher alcohol phosphate ester salt such as sodium phosphate ester of an alcohol having 6 or more carbon atoms; alkyl

sulfosuccinate; and the like. Among these anionic emulsifier, a phosphate ester salt and a sulfate ester salt are preferable, and a higher alcohol phosphate ester salt and a higher alcohol sulfate ester salt are more preferable. These anionic emulsifier may be used alone or in combination of two or more thereof.

Examples of the cationic emulsifier include alkyl trimethyl ammonium chloride, dialkyl ammonium chloride, benzyl ammonium chloride and the like.

[0034] These emulsifier may be used alone or in combination of two or more thereof, and among them, a nonionic emulsifier and an anionic emulsifier are preferred, and a nonionic emulsifier and an anionic emulsifier are more preferably used in combination. By using the nonionic emulsifier and the anionic emulsifier in combination, it is possible to reduce the amount of coagulant used in coagulation step described later while effectively preventing the occurrence of foulings due to adhesion of a polymer and the like to a polymerization device (e.g., a polymerization tank) during emulsion polymerization. As a result, it is possible to reduce the amount of coagulant in the acrylic rubber finally obtained, thereby improving the water resistance of the cross-linked rubber obtained. Further, by using the nonionic emulsifier and the anionic emulsifier in combination, it is possible to enhance the emulsifying action, so that it is possible to also reduce the amount of emulsifier itself to be used, and as a result, it is possible to reduce the residual amount of emulsifier contained in the acrylic rubber finally obtained, thereby further enhancing the water resistance of the obtained acrylic rubber.

[0035] The amount of emulsifier to be used is usually in the range of 0.01 to 10 parts by weight, preferably in the range of 0.1 to 5 parts by weight, and more preferably in the range of 1 to 3 parts by weight, with respect to 100 parts by weight of the monomer used in the

polymerization. In addition, when the nonionic emulsifier and the anionic emulsifier are used in combination, the weight ratio of nonionic emulsifier/anionic emulsifier is usually from 1/99 to 99/1, preferably from 10/90 to 80/20, more preferably from 25/75 to 75/25, still more preferably from 50/50 to 75/25, and most preferably from 65/35 to 75/25. By setting the weight ratio to the range above, the effect of the present invention is highly enhanced, and thus is suitable for achieving the purpose of the invention of the present application.

[0036] As a polymerization initiator, an azo compound such as azobisisobutyronitrile; an organic peroxide such as diisopropylbenzene hydroperoxide, cumene hydroperoxide, paramenthane hydroperoxide, and benzoyl peroxide; an inorganic peroxide such as sodium persulfate, potassium persulfate, hydrogen peroxide, and ammonium persulfate; and the like can be used. These polymerization initiators may be used alone or in combination of two or more thereof. The amount of the polymerization initiator to be used is usually in the range of 0.001 to 5 parts by weight, preferably 0.01 to 1 parts by weight, and more preferably 0.05 to 0.5 parts by weight, with respect to 100 parts by weight of the monomer used in the polymerization.

[0037] The peroxides such as the organic peroxides and/or inorganic peroxides as the polymerization initiator are preferably used as a redox polymerization initiator in combination with a reducing agent. Any reducing agent can be used in combination. Examples thereof include reduced metal ion-containing compounds, such as ferrous sulfate, hexamethylenediaminetetraacetic acid ferric sodium salt, and cuprous naphthenate; ascorbic acid (salts) such as ascorbic acid, sodium ascorbate, and potassium ascorbate; erythorbic acid (salts) such as erythorbic acid, sodium erythorbate, and potassium erythorbate; saccharides; sulfinic acid salts such as sodium hydroxymethanesulfinate; sulfurous acid salts such as sodium sulfite, potassium sulfite, sodium

hydrogen sulfite, aldehyde sodium hydrogen sulfite, and potassium hydrogen sulfite; pyrosulfurous acid salts such as sodium pyrosulfite, potassium pyrosulfite, sodium hydrogen pyrosulfite, and potassium hydrogen pyrosulfite; thiosulfuric acid salts such as sodium thiosulfate and potassium thiosulfate; phosphorus acid (salts) such as phosphorus acid, sodium phosphite, potassium phosphite, sodium hydrogen phosphite, and potassium hydrogen phosphite; pyrophosphorus acid (salts) such as pyrophosphorus acid, sodium pyrophosphite, potassium pyrophosphite, sodium hydrogen pyrophosphite, and potassium hydrogen pyrophosphite; and sodium formaldehyde sulfoxylate; and the like.

[0038] These reducing agents may be used alone or in combination of two or more thereof, respectively, but by combining a metal ion-containing compound which is in a reduced state as a first reducing agent with another reducing agent as a second reducing agent, preferably by combining ferrous sulfate with ascorbic acid (salt) and/or sodium formaldehyde sulfoxylate, and particularly preferably by combining ferrous sulfate with ascorbate, it is possible to highly enhance the water resistance and the compression set resistance property when the obtained acrylic rubber is made into a cross-linked product, which is suitable. The amount of the reducing agent to be used is preferably in the range of 0.00001 to 1 parts by weight, more preferably 0.0001 to 0.5 parts by weight, with respect to 100 parts by weight of the monomer used in the polymerization. When ferrous sulfate and ascorbic acid (salt) are used in combination, the amount of ferrous sulfate used is usually in the range of 0.00001 to 0.01 parts by weight, preferably 0.0001 to 0.001 parts by weight, and the amount of ascorbic acid (salt) used is usually in the range of 0.001 to 5 parts by weight, preferably 0.01 to 1 parts by weight, with respect to 100 parts by weight of the monomer used in the polymerization.

[0039] The amount of water to be used is preferably 80 to 500 parts

by weight, more preferably 100 to 300 parts by weight with respect to 100 parts by weight of the monomers used in polymerization.

[0040] In emulsion polymerization, polymerization additives such as a molecular weight adjuster, a particle size adjuster, a chelating agent, and an oxygen trapping agent can be used as needed.

[0041] Although emulsion polymerization may be performed by any of a batchwise method, a semi-batchwise method, and a continuous method, a semi-batchwise method is preferred. Specifically, it is preferred that the polymerization reaction be performed while at least one selected from the monomers used in polymerization, the polymerization initiator, and the reducing agent is being continuously added dropwise to the polymerization reaction system from the start of the polymerization reaction to any point of time. For example, the polymerization reaction is performed while the monomers used in polymerization are being continuously added dropwise to a polymerization reaction system containing the polymerization initiator and the reducing agent from the start of the polymerization reaction to any point of time. It is more preferred that the polymerization reaction be performed while all the monomers used in polymerization, the polymerization initiator, and the reducing agent are being continuously added dropwise to the polymerization reaction system from the start of the polymerization reaction to any point of time. By performing the polymerization reaction while these substances are being continuously added dropwise, the emulsion polymerization can be stably performed, improving the polymerization conversion ratio. The polymerization is performed in the temperature range of usually 0 to 70°C, preferably 5 to 50°C.

[0042] In addition, when a polymerization reaction is performed while continuously dropping a monomer used for polymerization, it is preferable that a monomer used for polymerization is mixed with an emulsifier and water to obtain a monomer emulsion (an emulsion

preparation step), and continuously dropped in a state of the monomer emulsion. In other words, it is preferable to set a configuration further comprising: an emulsion preparation step in which a monomer for forming an acrylic rubber, which is used for polymerization, is pre-mixed with an emulsifier and water to obtain a monomer emulsion; and polymerizing a monomer contained in such a monomer emulsion while continuously dropping into the polymerization reaction system in the subsequent emulsion polymerization step. The monomer emulsion can be prepared by any method. Examples thereof include a method of stirring the total amount of the monomers used in polymerization, the total amount of the emulsifiers, and water with a stirrer such as a homomixer and a disc turbine. The amount of water to be used in the monomer emulsion is preferably 10 to 70 parts by weight, more preferably 20 to 50 parts by weight, with respect to 100 parts by weight of the monomers used in polymerization.

[0043] If the polymerization reaction is performed while all the monomers used in polymerization, the polymerization initiator, and the reducing agent are being continuously added dropwise to the polymerization reaction system from the start of the polymerization reaction to any point of time, these substances may be separately added dropwise to the polymerization system using droppers, or at least the polymerization initiator and the reducing agent may be preliminarily mixed and prepared into an aqueous solution as needed, so that these agents may be added dropwise to the polymerization system from the same dropper. After the addition is completed, the reaction may be continued for any time to further improve the polymerization conversion ratio.

[0044] The termination of the emulsion polymerization can be carried out by adding a polymerization terminator if necessary. Examples of the polymerization terminator include hydroxylamine, hydroxylamine sulfate, diethylhydroxylamine, hydroxylamine sulfonic acid and an alkali metal salt

thereof, sodium dimethyldithiocarbamate, and hydroquinone. The polymerization terminator can be used in any amount. The amount thereof is preferably 0.1 to 2 parts by weight with respect to 100 parts by weight of the monomers used in polymerization.

[0045] <Coagulation step>

The coagulation step in the production method of the present invention is characterized in that the above-mentioned polymerized emulsion liquid is coagulated in the presence of two or more types of compounds having a polyoxyalkylene skeleton to obtain a hydrous crumb.

[0046] The method for coagulating a polymerized emulsion liquid obtained by emulsion polymerization step is not particularly limited as long as it is in accordance with a conventional method, but can be carried out, for example, by contacting a polymerized emulsion liquid with a coagulant. A method of bringing a polymerized emulsion liquid and a coagulant into contact with each other to coagulate is not particularly limited, and examples thereof include a method for adding a coagulant in a polymerized emulsion liquid and a method for forming an aqueous solution by dissolving a coagulant in water and adding a polymerized emulsion liquid to the aqueous solution of this coagulant.

[0047] In addition, a method for performing coagulation in the presence of two or more types of compounds having a polyoxyalkylene skeleton is not particularly limited, and examples thereof include a method comprising: adding two or more types of compounds having a polyoxyalkylene skeleton in a polymerized emulsion liquid obtained in the emulsion polymerization step in advance; and adding a coagulant in such a polymerized emulsion liquid, and a method comprising: dissolving a coagulant in water to form an aqueous solution; preliminary adding two or more types of compounds having a polyoxyalkylene skeleton in the aqueous solution of this coagulant; and adding a polymerized emulsion liquid to the aqueous solution of the coagulant thus obtained.

Alternatively, the examples may include a method comprising: adding at least a portion of the two or more types of compounds having a polyoxyalkylene skeleton in polymerized emulsion liquid in advance; and adding the remaining portion of the two or more types of compounds having a polyoxyalkylene skeleton in an aqueous solution of coagulant. Among these, it is preferable to that a polymerized emulsion liquid obtained in the emulsion polymerization step contains two or more different types of compounds having a polyoxyalkylene skeleton in view of more appropriately enhancing the action and effect of the present invention.

[0048] The compound having a polyoxyalkylene skeleton is not particularly limited, and examples thereof include a polyalkylene glycol (A), an ester compound of a polyalkylene glycol (B1) and/or an ether compound of a polyalkylene glycol (B2), and the like.

[0049] As the polyalkylene glycol (A), there is no particular limitation as long as it is a polymer of an alkylene oxide having a polyoxyalkylene skeleton, but a polymer of a lower alkylene oxide is suitably used. Examples of the polyalkylene glycol include homopolymers of oxyalkylene such as polyethylene glycol (polyethylene oxide), polypropylene glycol (polypropylene oxide), and polyoxyethylene polyoxypropylene glycol (ethylene oxide/propylene oxide copolymer), and among them, polyethylene glycol (polyethylene oxide) is suitable.

[0050] The weight average molecular weight (Mw) of the polyalkylene glycol (A) is not particularly limited, but is usually in the range of 1,000 to 5,000,000, preferably in the range of 10,000 to 1,000,000, more preferably in the range of 50,000 to 500,000, and most preferably in the range of 70,000 to 300,000.

[0051] As the ester compound of polyalkylene glycol (B1) and/or the ether compound of polyalkylene glycol (B2), there is no particular limitation as long as it is an ester compound, an ether compound, or an

ester and ether compound of the polyalkylene glycol, for example, at least one polyoxyalkylene ester compound selected from the group consisting of polyoxyalkylene phosphoric ester, polyoxyalkylene sulfate ester, polyoxyalkylene fatty acid ester and other polyoxyalkylene ether esters, and/or at least one polyoxyalkylene ether compound having no ester group selected from the group consisting of polyoxyalkylene alkyl ether and polyoxyalkylene aryl ether are suitably used.

As the polyoxyalkylene ester compound, a polyoxyalkylene phosphate ester and a polyoxyalkylene fatty acid ester are particularly preferred.

[0052] Examples of the polyoxyalkylene phosphate include polyoxyethylene stearyl ether phosphate, polyoxyethylene lauryl ether phosphate, polyoxyethylene oleyl ether phosphate, and polyoxyethylene tridecyl ether phosphate.

[0053] Examples of the polyoxyalkylene fatty acid ester include polyoxyethylene monostearic acid ester, polyoxyethylene monolauric acid ester, polyoxyethylene monooleic acid ester, polyoxyethylene sorbitan lauric acid ester, polyoxyethylene sorbitan stearic acid ester, polyoxyethylene sorbitan oleic acid ester, and polyoxyethylene sorbitan palmitic acid ester, and the like. Among these, polyoxyethylene monostearic acid ester is preferred.

[0054] Examples of the polyoxyalkylene alkyl ether include polyoxyethylene dodecyl ether, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene myristyl ether, polyoxyethylene octyl dodecyl ether, polyoxyethylene polyoxypropylene cetyl ether, and polyoxyethylene polyoxypropylene decyl tetradecyl ether. Among these, polyoxyethylene dodecyl ether is preferred.

[0055] Examples of the polyoxyalkylene aryl ether include polyoxyethylene nonylphenyl ether and polyoxyethylene octylphenyl ether.

Among these, polyoxyethylene nonylphenyl ether is preferred.

[0056] The weight average molecular weight (Mw) of the ester compound of the polyalkylene glycol (B1) and/or the ether compound of the polyalkylene glycol (B2) is not particularly limited, but is usually in the range of 100 to 30,000, preferably in the range of 200 to 15,000, more preferably in the range of 300 to 10,000, and most preferably in the range of 400 to 8,000.

[0057] Note that, in the production method of the present invention, coagulation may be performed in the presence of two or more types of compounds having a polyoxyalkylene skeleton, and the type of the two or more compounds having a polyoxyalkylene skeleton used at this time is not particularly limited, but at least one kind of compound among the above-described polyalkylene glycol (A), the ester compound of the polyalkylene glycol (B1) and/or the ether compound of the polyalkylene glycol (B2) is preferably used. In other words, any one of the above-described compound and a compound having a polyoxyalkylene skeleton other than the above-described compound may be used in combination, or two or more of the above-described compounds may be used in combination.

[0058] In addition, in the method for producing the present invention, two or more kinds of compounds having a polyoxyalkylene skeleton having different molecular weights are preferably used as the compound having two or more kinds of compounds having a polyoxyalkylene skeleton from the viewpoint of further enhancing the action and effect of the present invention, and among them, it is more suitable to use a low molecular weight compound (α 1) having a weight average molecular weight (Mw) of less than 10000 and a polymer compound (α 2) having a weight average molecular weight (Mw) of 10000 or more in combination.

[0059] The weight average molecular weight (Mw) of the low molecular weight compound (α 1) having a polyoxyalkylene skeleton is preferably in the range of 100 to 8,000, more preferably in the range of 200 to 7,000,

particularly preferably in the range of 300 to 6,000, and most preferably in the range of 400 to 5,000. The low molecular weight compound ($\alpha 1$) having a polyoxyalkylene skeleton may be any one of a polyalkylene glycol (A), an ester compound of a polyalkylene glycol (B1), and an ether compound of a polyalkylene glycol (B2), but is preferably an ester compound of a polyalkylene glycol (B1) or an ether compound of a polyalkylene glycol (B2), and more preferably a phosphate ester compound of a polyalkylene glycol, a fatty acid ester compound of a polyalkylene glycol that is not esterified with a phosphoric acid, or a fatty acid ether compound of a polyalkylene glycol that is not esterified with a phosphoric acid, and most preferably an ether compound of a polyalkylene glycol. With regard to the low molecular weight compound ($\alpha 1$) having a polyoxyalkylene skeleton, by selecting the above-mentioned compound within the weight-average molecular weight (M_w) range mentioned above, the effect of the present invention is remarkably enhanced and thus is suitable. These low molecular weight compounds ($\alpha 1$) having a polyoxyalkylene skeleton may be used alone or in combination of two or more thereof.

[0060] The weight average molecular weight (M_w) of the high molecular weight compound ($\alpha 2$) having a polyoxyalkylene skeleton is preferably in the range of 20,000 to 6,000,000, more preferably in the range of 40,000 to 2,000,000, particularly preferably in the range of 50,000 to 500,000, and most preferably in the range of 60,000 to 300,000. The high molecular weight compound ($\alpha 2$) having a polyoxyalkylene skeleton may be any one of a polyalkylene glycol (A), an ester compound of a polyalkylene glycol (B1) and an ether compound of a polyalkylene glycol (B2), but is preferably a polyalkylene glycol (A). With regard to the high molecular weight compound ($\alpha 2$) having a polyoxyalkylene skeleton, by selecting the above-mentioned compound within the weight-average molecular weight (M_w) range mentioned above,

the effect of the present invention is remarkably enhanced and thus is suitable. These high molecular weight compounds ($\alpha 2$) having a polyoxyalkylene skeleton may be used alone or in combination of two or more thereof.

[0061] The content of the low molecular weight compound ($\alpha 1$) having a polyoxyalkylene skeleton in a polymerized emulsion liquid is appropriately selected depending on an intended use, but is usually in the range of 0.01 to 15 parts by weight, preferably in the range of 0.1 to 10 parts by weight, and more preferably in the range of 0.5 to 5 parts by weight, with respect to 100 parts by weight of the acrylic rubber ingredient in a polymerized emulsion liquid.

[0062] The content of the high molecular weight compound ($\alpha 2$) having a polyoxyalkylene skeleton in a polymerized emulsion liquid is appropriately selected depending on an intended use, but is usually in the range of 0.0001 to 1 parts by weight, preferably in the range of 0.001 to 0.1 parts by weight, and more preferably in the range of 0.005 to 0.05 parts by weight, with respect to 100 parts by weight of the acrylic rubber ingredient in a polymerized emulsion liquid.

[0063] The ratio of the low molecular weight compound ($\alpha 1$) having a polyoxyalkylene skeleton and the high molecular weight compound ($\alpha 2$) having a polyoxyalkylene skeleton is not particularly limited, but is usually in the range of 30/70 to 99.9999/0.0001, preferably in the range of 50/50 to 99.999/0.001, more preferably in the range of 70/30 to 99.99/0.01, still more preferably in the range of 80/20 to 99.95/0.05, and most preferably in the range of 90/10 to 99.9/0.1, in terms of the weight ratio of the low molecular weight compound ($\alpha 1$)/the high molecular weight compound ($\alpha 2$) having a polyoxyalkylene skeleton.

[0064] Alternatively, in the production method of the present invention, as two or more types of compounds having a polyoxyalkylene skeleton, a polyalkylene glycol (A) and an ester compound of a

polyalkylene glycol (B1) and/or an ether compound of a polyalkylene glycol (B2) may be used in combination. Even in this case, the action and effect of the present invention can be further enhanced, which is preferable.

[0065] When these are used in combination, each of the polyalkylene glycol (A) may be used alone or in combination of two or more thereof, and the amount thereof added is not particularly limited, but is usually in the range of 0.0001 to 1 parts by weight, preferably in the range of 0.001 to 0.1 parts by weight, and more preferably in the range of 0.005 to 0.05 parts by weight, with respect to 100 parts by weight of the acrylic rubber ingredient in a polymerized emulsion liquid. Further, the ester compound of the polyalkylene glycol (B1) and/or the ether compound of the polyalkylene glycol (B2) may be used alone or in combination of two or more thereof, and the amount thereof added is appropriately selected depending on an intended use, but is usually in the range of 0.01 to 15 parts by weight, preferably in the range of 0.1 to 10 parts by weight, and more preferably in the range of 0.5 to 5 parts by weight, with respect to 100 parts by weight of the acrylic rubber ingredient in a polymerized emulsion liquid.

[0066] Although there is no particular limitation on the ratio of a polyalkylene glycol (A), and an ester compound of a polyalkylene glycol (B1) and/or an ether compound of a polyalkylene glycol (B2), it is usually in the range of 30/70~99.9999/0.0001, preferably in the range of 50/50~99.999/0.001, more preferably in the range of 70/30~99.99/0.01, and still more preferably in the range of 80/20~99.95/0.05, and most preferably in the range of 90/10 to 99.9/0.1 in terms of "polyalkylene glycol (A)/ester compound of polyalkylene glycol (B1) and/or ether compound of polyalkylene glycol (B2)".

[0067] The coagulant is not particularly limited, and examples thereof include monovalent, bivalent, and trivalent (hereinafter

referred to as "1 to 3 valent") metallic salts. The 1 to 3 valent metal salt is a salt containing a metal which becomes a 1 to 3 valent metal ion when dissolved in water, and is not particularly limited, and examples thereof include a salt of an inorganic acid such as hydrochloric acid, nitric acid and sulfuric acid and an organic acid such as an acetic acid, and a metal selected from sodium, potassium, lithium, magnesium, calcium, zinc, titanium, manganese, iron, cobalt, nickel, aluminum, tin, and the like. Hydroxides of these metals can also be used.

[0068] Examples of the 1 to 3 valent metal salt include a metal chloride such as sodium chloride, potassium chloride, lithium chloride, magnesium chloride, calcium chloride, zinc chloride, titanium chloride, manganese chloride, iron chloride, cobalt chloride, nickel chloride, aluminum chloride, tin chloride; a metal nitrate such as sodium nitrate, potassium nitrate, lithium nitrate, magnesium nitrate, calcium nitrate, zinc nitrate, titanium nitrate, manganese nitrate, iron nitrate, cobalt nitrate, nickel nitrate, aluminum nitrate, tin nitrate; a metal sulfate such as sodium sulfate, potassium sulfate, lithium sulfate, magnesium sulfate, calcium sulfate, zinc sulfate, titanium sulfate, manganese sulfate, iron sulfate, cobalt sulfate, nickel sulfate, aluminum sulfate and tin sulfate; and the like. Among these, a metal chloride and a metal sulfate are preferred, a monovalent or bivalent metal chloride and a monovalent or bivalent metal sulfate are more preferred, and a monovalent or bivalent metal sulfate is particularly preferred. As the monovalent or bivalent metal salt, calcium chloride, sodium chloride, magnesium sulfate, and sodium sulfate are preferred, and magnesium sulfate and sodium sulfate are more preferred. Among these, the effect of the present invention is highly enhanced when a sulfate, particularly a monovalent or bivalent metallic sulfate, is used, which is suitable.

[0069] These coagulants may be used alone or in combination of two

or more thereof. The amount of the coagulant to be used (contained) is usually in the range of 0.01 to 100 parts by weight, preferably in the range of 0.1 to 50 parts by weight, and more preferably in the range of 1 to 30 parts by weight, with respect to 100 parts by weight of the acrylic rubber ingredient in a polymerized emulsion liquid. It is preferable to set the amount of coagulant within these ranges since it enables to highly improve compression set resistance and water resistance of the cross-linked acrylic rubber while the coagulation of the acrylic rubber is sufficiently maintained.

[0070] The method for contacting a polymerized emulsion liquid with a coagulant may be performed according to a conventional method, and may be performed by adding a coagulant to a polymerized emulsion liquid or adding a polymerized emulsion liquid into a coagulant solution. When adding a polymerized emulsion liquid to a coagulant solution, an aqueous solution is usually used, and a coagulant concentration is appropriately selected, and is usually in the range of 1 to 40 wt%, preferably in the range of 5 to 30 wt%, and more preferably in the range of 10 to 25 wt%. In addition, when adding a coagulant to a polymerized emulsion liquid, a coagulant may be a powdery solid or may be dissolved and added as an aqueous solution. When adding a coagulant as an aqueous solution, the coagulant concentration is appropriately selected depending on an intended use, and is usually in the range of 1 to 50 wt%, preferably in the range of 5 to 40 wt%, and more preferably in the range of 10 to 30 wt%.

[0071] A coagulation temperature of a polymerized emulsion liquid is a temperature at which a polymerized emulsion liquid and a coagulant come into contact with each other when coagulant is used, and is not particularly limited, but is usually 60 °C or more, preferably 70 to 95 °C, and more preferably 78 to 90 °C. Since a compound having a polyoxyalkylene skeleton greatly affects the coagulation reaction due to

temperature, it is suitable to bring the coagulation (contacting) temperature into these ranges.

[0072] In addition, in the production method of the present invention, it is preferable that a part of a compounding agent to be composed in the acrylic rubber (e.g., antioxidant) is contained in advance in a polymerized emulsion liquid before coagulation is performed. In other words, with regard to an antioxidant, it is preferable to set a state in which an antioxidant is already contained in a polymerized emulsion liquid, and to perform coagulation with a polymerized emulsion liquid to which the antioxidant has been composed.

[0073] For example, by containing an antioxidant in advance in a polymerized emulsion liquid prior to performing coagulation, it is possible to effectively prevent deterioration of the acrylic rubber due to heat when drying in a drying step described later. Specifically, it is possible to effectively prevent a decrease in a Mooney viscosity caused by deterioration due to heating during drying, and thereby, it is possible to effectively enhance a normal tensile strength, an elongation at break, and the like when the acrylic rubber is formed into a cross-linked rubber. In addition, by composing an antioxidant in the state of a polymerized emulsion liquid prior to performing coagulation, the antioxidant can be appropriately dispersed, so that even when the composition amount of antioxidant is reduced, the effect of addition can be sufficiently exhibited. Specifically, even the composition amount of an antioxidant is relatively small, preferably from 0.1 to 2 parts by weight, more preferably from 0.2 to 1.2 parts by weight, with respect to 100 parts by weight of the acrylic rubber ingredient in a polymerized emulsion liquid, the effect of addition can be sufficiently exhibited. Note that, even when an antioxidant is contained in a polymerized emulsion liquid prior to performing coagulation, the added antioxidant is not substantially removed in the subsequent coagulation, washing,

drying, and the like, so that the effect of addition can be sufficiently exhibited. Further, a method for containing an antioxidant in a polymerized emulsion liquid includes a method for adding an antioxidant to a polymerized emulsion liquid after emulsion polymerization and before performing coagulation, and a method for adding an antioxidant to a solution before performing emulsion polymerization. When adding an antioxidant to a solution before performing emulsion polymerization, since aggregates are generated during the emulsion polymerization, which may cause stains of the polymerization apparatus, it is preferable to add an antioxidant to a polymerized emulsion liquid after emulsion polymerization and before performing coagulation. Examples of an antioxidant include, but are not limited to, those described later.

[0074] <Washing step>

In the production method of the present invention, it is preferable to further comprise a washing step of performing washing on a hydrous crumb obtained in the above-described coagulation step.

[0075] Any washing method can be used without limitation. Examples thereof include a method of washing hydrous crumbs with water by using water as a washing liquid, and mixing the hydrous crumbs with added water. The operation to wash hydrous crumbs with water can be performed at any temperature without limitation. The temperature is preferably 5 to 60°C, more preferably 10 to 50°C, and the mixing time is 1 to 60 minutes, more preferably 2 to 30 minutes.

[0076] Further, when washing with water, the amount of water added to a hydrous crumb is not particularly limited, but is preferably from 50 to 9,800 parts by weight, more preferably from 300 to 1,800 parts by weight, with respect to 100 parts by weight of solid content (mainly, acrylic rubber ingredient) contained in a hydrous crumb, from the viewpoint that the residual amount of a coagulant in the acrylic rubber finally obtained can be effectively reduced.

[0077] The number of times of washing with water is not particularly limited, and may be one time, but may be a plurality of times from the viewpoint of reducing the residual amount of a coagulant in the acrylic rubber finally obtained, and is preferably 2 to 10 times, more preferably 3 to 8 times. Noted that, from the viewpoint of reducing the residual amount of a coagulant in the acrylic rubber finally obtained, it is desirable that the number of times of washing with water is larger. However, even the washing is performed beyond the above range, the effect of removing a coagulant is small, while the effect of lowering productivity becomes large due to the increase in the number of steps. Therefore, the number of times of washing with water is preferably set within the above range.

[0078] In the present invention, after washing with water, acid washing may be further performed with using an acid as a washing liquid. By performing acid washing, it is possible to highly enhance storage stability of the acrylic rubber, and further to enhance compression set resistance when the acrylic rubber is cross-linked to be formed into a cross-linked rubber, which is suitable.

[0079] Any acid, such as sulfuric acid, hydrochloric acid, and phosphoric acid, can be used without limitation. In addition, when adding an acid to a hydrous crumb in acid washing, it is preferable to add the acid in a state of an aqueous solution. A pH of the acid is usually 6 or less, preferably 5 or less, more preferably 4 or less, and most preferably 3 or less. The lower limit value of the pH is not particularly limited, but is usually 1 or more. When an acid concentration is in these ranges, the effect of improving the storage stability and the compression set resistance is maximized, which is preferable. In addition, the pH at that time is usually 6 or less, preferably 5 or less, and more preferably 4 or less. Note that, the pH of washing water in the acid washing can be determined, for example, by

measuring a pH of water contained in a hydrous crumb after the acid washing.

[0080] The acid washing can be performed at any temperature. The temperature is preferably 5 to 60 °C, more preferably 10 to 50 °C, and the mixing time is 1 to 60 minutes, more preferably 2 to 30 minutes.

After acid washing is performed, it is preferred that washing with water be further performed. The same conditions as those in washing with water can be used.

[0081] <Drying step>

Further, in the production method of the present invention, it is preferable to further comprise a drying step of performing drying on a hydrous crumb subjected to washing in the above washing step.

[0082] In the drying step, the drying method is not particularly limited, and may be dried with using, for example, a dryer such as a screw type extruder, a kneader type dryer, an expander dryer, a hot air dryer, a vacuum dryer, and the like. A drying method using a combination thereof may also be used. Furthermore, before drying of a hydrous crumb in the drying step, the hydrous crumb may be separated, as needed, with using a sieve such as a rotary screen and a vibration screen; a centrifugal dehydrator; and the like.

For example, a drying temperature in the drying step is not particularly limited and varies depending on a dryer used for drying. For example, when a hot air dryer is used, the drying temperature is preferably 80 to 200 °C, and more preferably 100 to 170 °C.

[0083] [Acrylic rubber]

Thus, the acrylic rubber obtained by the above production method of the present invention can effectively prevent the generation of the mutual adhesion between hydrous crumbs, is recovered in a high polymer recovery ratio, is excellent in roll processability, and provides a cross-linked rubber that has excellent water resistance.

[0084] There is no particular limitation on the acrylic rubber of the present invention except that it contains a (meth)acrylic acid ester unit as a main component. And, when further containing a cross-linkable monomer unit, it is excellent in water resistance and compression set resistance, and thus is suitable.

[0085] The monomer composition in the acrylic rubber of the present invention is appropriately selected depending on an intended use, but the (meth)acrylic acid ester unit is usually in the range of 50 to 99.9 wt%, preferably in the range of 60 to 99.7 wt%, more preferably in the range of 70 to 99.5 wt%. The content of the cross-linkable monomer unit is usually in the range of 0.01 to 20 wt%, preferably in the range of 0.1 to 10 wt%, and more preferably in the range of 0.5 to 5 wt%. The content of the other copolymerizable monomer unit is usually in the range of 0 to 49.99 wt%, preferably in the range of 0 to 39.9 wt%, and more preferably in the range of 0 to 29.5 wt%. Examples of the (meth)acrylic acid ester, the cross-linkable monomer and other copolymerizable monomers are the same as those of "<monomer>" as mentioned above. The cross-linkable monomer unit includes a carboxyl group-containing monomer unit, a halogen group-containing monomer unit, an epoxy group-containing monomer unit, and the like, and a carboxyl group-containing monomer unit is particularly preferred.

[0086] The Mooney viscosity (ML1+4, 100 °C) of the acrylic rubber according to the present invention is selected depending on the intended use, but is usually in the range of 10 to 150, preferably in the range of 10 to 100, more preferably in the range of 10 to 80, still more preferably in the range of 20 to 80, and particularly preferably in the range of 25 to 60.

[0087] The glass transition temperature (T_g) of the acrylic rubber according to the present invention is selected depending on the intended use, but is usually 25 °C or less, preferably 15 °C or less, and more

preferably 0 °C or less.

[0088] According to the present invention, there is provided a method for producing the acrylic rubber, and an acrylic rubber obtained by the production method.

[0089] In particular, according to the acrylic rubber of the present invention obtained by the above production method, in addition to being excellent in roll processability and water resistance, the generation of blocking of hydrous crumbs is effectively prevented. In the field of rubber such as acrylic rubber, coagulation is usually performed when a solid rubber is obtained from a solution or a dispersion of rubber obtained by polymerization, and a rubber such as acrylic rubber is obtained in the form of a hydrous crumb by such coagulation. On the other hand, according to the present invention, it is possible to provide an acrylic rubber in which the generation of the mutual adhesion in such a form of hydrous crumb is effectively prevented.

[0090] Note that, as described above, a hydrous crumb is obtained by coagulation, and therefore, whether the mutual adhesion between hydrous crumb is observed is greatly affected by a coagulation condition and the state at the time of coagulation. On the other hand, the acrylic rubber of the present invention is obtained by coagulation in the presence of two or more types of compounds having a polyoxyalkylene skeleton. The acrylic rubber obtained by such coagulation includes two or more types of compounds having a polyoxyalkylene skeleton and a coagulant, but according to the findings of the present inventors, it is not possible to prevent such generation of mutual adhesion by simply including the compounds having a polyoxyalkylene skeleton and a coagulant. It has been found that it is necessary to carry out the coagulation in the presence of two or more types of compounds having a polyoxyalkylene skeleton. The acrylic rubber of the present invention is obtained first time ever with such a coagulation process, and cannot be generally specified by simply

the term that two or more types of compounds having a polyoxyalkylene skeleton and a coagulant are included.

[0091] Further, with respect to the acrylic rubber of the present invention, if the internal state thereof is analyzed by using various analytical instruments, both the acrylic rubber and the two or more types of compounds having a polyoxyalkylene skeleton include a carbon atom and an oxygen atom as a main component, and it is extremely difficult to specify its dispersion state and the like. Therefore, it can be said that it is sufficiently reasonable to specify the acrylic rubber of the present invention by the production method.

[0092] [Rubber composition]

The rubber composition of the present invention comprises a rubber ingredient and a cross-linking agent, the rubber ingredient comprising the above acrylic rubber. The content of the acrylic rubber of the present invention in a rubber ingredient may be selected depending on the intended use, and is, for example, usually 30 wt% or more, preferably 50 wt% or more, and more preferably 70 wt% or more.

[0093] As a rubber ingredient, the above-mentioned acrylic rubber alone or in combination with the above-mentioned acrylic rubber and other rubber can be used.

[0094] The other rubber include acrylic rubber other than the acrylic rubbers of the present invention, natural rubbers, polybutadiene rubbers, polyisoprene rubbers, styrene-butadiene rubbers, acrylonitrile-butadiene rubbers, silicon rubbers, fluororubber, olefinic elastomers, styrene-based elastomers, vinyl chloride-based elastomers, polyester-based elastomers, polyamide-based elastomers, polyurethane-based elastomers, polysiloxane-based elastomers, and the like.

[0095] These other rubbers may be used alone or in combination of two or more thereof. The content of the other rubber in a rubber ingredient is appropriately selected within a range not impairing the

effect of the present invention, and is, for example, usually 70 wt% or less, preferably 50 wt% or less, and more preferably 30 wt% or less.

[0096] The cross-linking agent used in the rubber composition of the present invention is not particularly limited, and may be a conventionally known cross-linking agent such as, for example, a polyvalent amine compound such as a diamine compound, and a carbonate thereof; a sulfur compound; a sulfur donor; a polyvalent epoxy compound; an organic carboxylic acid ammonium salt; an organic peroxide; a polyvalent carboxylic acid; an isocyanuric acid compound; an organic peroxide; a triazine compound; and the like. Among these, a polyvalent amine compound and a triazine compound are preferred, and a polyvalent amine compound is particularly preferred.

[0097] Examples of the polyvalent amine compound include an aliphatic polyvalent amine compound such as Hexamethylenediamine, hexamethylenediamine carbamate, N,N'-dicinnamylidene-1,6-hexanediamine; an aromatic polyvalent amine compound such as 4,4'-methylenedianiline, p-phenylenediamine, m-phenylenediamine, 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-(m-phenylenediisopropylidene)dianiline, 4,4'-(p-phenylenediisopropylidene)dianiline, 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, 4,4'-diaminobenzanilide, 4,4'-bis(4-aminophenoxy)biphenyl, m-xylylenediamine, p-xylylenediamine, 1,3,5-benzenetriamine; and the like. Among these, hexamethylenediamine carbamate and 2,2'-bis[4-(4-aminophenoxy)phenyl]propane are preferred. These polyvalent amine compounds are particularly suitably used in combination with an acrylic rubber containing a carboxyl group.

[0098] Examples of the triazine compound include 6-trimercapto-s-triazine, 2-anilino-4,6-dithiol-s-triazine, 1-dibutylamino-3,5-dimercaptotriazine, 2-dibutylamino-4,6-dithiol-s-triazine, 1-phenylamino-3,5-dimercaptotriazine, 2,4,6-trimercapto-1,3,5-triazine, 1-hexylamino-3,5-dimercaptotriazine, and the like. These triazine

compounds are particularly suitably used in combination with an acrylic rubber containing a halogen group.

[0099] These cross-linking agents may be used alone or in combination of two or more thereof, and the compounding amount thereof is usually in the range of 0.001 to 20 parts by weight, preferably in the range of 0.1 to 10 parts by weight, and more preferably in the range of 0.1 to 5 parts by weight, with respect to 100 parts by weight of rubber ingredient. By setting the compounding amount of a cross-linking agent to fall within these ranges, it is possible to make the mechanical strength as a cross-linked rubber excellent while making the rubber elasticity sufficient, which is suitable.

[0100] The rubber composition of the present invention can highly improve the effectiveness of the present invention by further comprising a cross-linking accelerator. The cross-linking accelerator is not particularly limited, and examples thereof include a guanidine-based cross-linking accelerator, a diazabicycloalkene-based cross-linking accelerator, an aliphatic secondary amine-based cross-linking accelerator, an aliphatic tertiary amine-based cross-linking accelerator, and a dithiocarbamate-based vulcanization accelerator as a suitable one. Among these, a guanidine-based cross-linking accelerator and a dithiocarbamate-based cross-linking accelerator are particularly preferred, and a guanidine-based cross-linking accelerator is more preferred.

[0101] Examples of the guanidine-based cross-linking accelerator include 1,3-diphenylguanidine (DPG), 1,3-di-o-tolylguanidine, 1-o-tolylbiguanide, dicatecholborate di-o-tolylguanidine salt, 1,3-di-o-cumenyl guanidine, 1,3-di-o-biphenylguanidine, 1,3-di-o-cumenyl-2-propionylguanidine, and the like. 1,3-diphenylguanidine 1,3-di-o-tolylguanidine and 1-o-tolylbiguanide are preferred because of their high reactivity, and 1,3-diphenylguanidine (DPG) is particularly

preferred because of its higher reactivity.

[0102] Examples of the diazabicycloalkene-based cross-linking accelerator include 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and the like.

[0103] Examples of the aliphatic secondary amine-based cross-linking accelerator include dimethylamine, diethylamine, dipropylamine, diallylamine, diisopropylamine, di-n-butylamine, di-t-butylamine, di-sec-butylamine, dihexylamine, diheptylamine, dioctylamine, dinonylamine, didecylamine, diundecylamine, didodecylamine, ditridecylamine, ditetradecylamine, dipentadecylamine, dicetylamine, di-2-ethylhexylamine, dioctadecylamine, and the like.

[0104] Examples of the aliphatic tertiary amine-based cross-linking accelerator include trimethylamine, triethylamine, tripropylamine, triallylamine, triisopropylamine, tri-n-butylamine, tri-t-butylamine, tri-sec-butylamine, trihexylamine, triheptylamine, trioctylamine, trinonylamine, tridecylamine, triundecylamine, tridodecylamine, and the like.

[0105] Examples of the dithiocarbamate-based cross-linking accelerator include zinc dimethyldithiocarbamate, zinc diethyldithiocarbamate, zinc dibutyldithiocarbamate, zinc dipentyldithiocarbamate, zinc dihexyldithiocarbamate, zinc N-pentamethylenedithiocarbamate, zinc N-ethyl-N-phenyldithiocarbamate, zinc dibenzoyldithiocarbamate, copper dipropyldithiocarbamate, copper diisopropyldithiocarbamate, copper dibutyldithiocarbamate, sodium diethyldithiocarbamate, sodium diisopropyldithiocarbamate, sodium dibutyldithiocarbamate, ferric dimethyldithiocarbamate, ferric diethyldithiocarbamate, and the like. Among these, zinc dimethyldithiocarbamate, zinc diethyldithiocarbamate, zinc dibutyldithiocarbamate, zinc dibenzoyldithiocarbamate, and zinc N-ethyl-N-phenyldithiocarbamate are preferred.

[0106] As the cross-linking accelerator used in the present invention, other cross-linking accelerators other than those described above may be used. Examples of other cross-linking accelerators include a sulfenamide cross-linking accelerator such as N-cyclohexyl-2-benzothiazyl sulfenamide, N-tert-butyl-2-benzothiazole sulfenamide, N-oxyethylene-2-benzothiazole sulfenamide, N-oxyethylene-2-benzothiazole sulfenamide, N.N-diisopropyl-2-benzothiazole sulfenamide; a thiourea-based cross-linking accelerator such as diethyl thiourea; a thiazole cross-linking accelerator such as 2-mercaptobenzothiazole, dibenzothiazyl disulfide, 2-mercaptobenzothiazole zinc salt; a xanthogenic acid cross-linking accelerator such as sodium isopropyl xanthate, zinc isopropyl xanthate, zinc butyl xanthate; a thiuram cross-linking accelerator such as tetramethylthiuram monosulfide and tetramethylthiuram disulfide; an imidazole-based cross-linking accelerator such as 2-methylimidazole and 2-phenylimidazole; a quaternary onium salt-based cross-linking accelerator such as tetra-n-butylammonium bromide, octadecyltri-n-butylammonium bromide; a tertiary phosphine-based cross-linking accelerators such as triphenylphosphine and tri-p-tolylphosphine; and the like.

[0107] These cross-linking accelerators may be used alone or in combination of two or more thereof, and the compounding amount thereof is usually in the range of 0.01 to 20 parts by weight, preferably in the range of 0.1 to 10 parts by weight, and more preferably in the range of 1 to 5 parts by weight, with respect to 100 parts by weight of rubber ingredient containing acrylic rubber. When content of the cross-linking accelerator is within these ranges, the tensile strength and compression set resistance of the obtained cross-linked rubber can be further improved, which is suitable.

[0108] The rubber composition of the present invention exhibits preferable cross-linked physical properties by further comprising a

scorch retarder, which is suitable. Examples of the scorch retarder include, but are not limited to, an imide compound such as N-cyclohexylthiophthalimide, an alkylamine alkylphenol compound, a hydroquinone quinone compound, 2,4-di(3-isopropylphenyl)-4-methyl-1-pentene, and the like, and an imide compound is preferred.

These scorch retarders may be used alone or in combination of two or more thereof, and the compounding amount thereof is in the range of 0.01 to 5 parts by weight, preferably in the range of 0.05 to 1 parts by weight, and more preferably in the range of 0.1 to 0.5 parts by weight, with respect to 100 parts by weight of rubber ingredient containing acrylic rubber.

[0109] It is preferable that the rubber composition of the present invention further contains an antioxidant. Any antioxidant can be used without limitation. Examples thereof include sulfur atom-free phenol antioxidants such as 2,6-di-*t*-butyl-4-methylphenol, 2,6-di-*t*-butylphenol, butylhydroxyanisole, 2,6-di-*t*-butyl- α -dimethylamino-*p*-cresol, octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, styrenated phenols, 2,2'-methylene-bis(6- α -methyl-benzyl-*p*-cresol), 4,4'-methylene-bis(2,6-di-*t*-butylphenol), 2,2'-methylene-bis(4-methyl-6-*t*-butylphenol), stearyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, alkylated bisphenol, and butylated reaction products of *p*-cresol and dicyclopentadiene; thiophenol antioxidants such as 2,4-bis[(octylthio)methyl]-6-methylphenol, 2,2'-thiobis-(4-methyl-6-*t*-butylphenol), 4,4'-thiobis-(6-*t*-butyl-*o*-cresol), and 2,6-di-*t*-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino)phenol; phosphorous acid ester antioxidants such as tris(nonylphenyl) phosphite, diphenylisodecyl phosphite, and tetraphenyldipropylene glycol·diphosphite; sulfur-containing ester antioxidants such as dilauryl thiodipropionate; amine antioxidants such as phenyl- α -naphthylamine, phenyl- β -naphthylamine, *p*-(*p*-toluenesulfonylamide)-diphenylamine, 4,4'-(α,α -

dimethylbenzyl)diphenylamine, N,N-diphenyl-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, and butylaldehyde-aniline condensates; imidazole antioxidants such as 2-mercaptobenzimidazole; quinoline antioxidants such as 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline; hydroquinone antioxidants such as 2,5-di-(t-amyl)hydroquinone; and the like.

[0110] These antioxidants may be used alone or in combination of two or more thereof, and the compounding amount thereof is in the range of 0.01 to 15 parts by weight, preferably from in the range of 0.1 to 10 parts by weight, and more preferably in the range of 1 to 5 parts by weight, with respect to 100 parts by weight of rubber ingredient containing acrylic rubber.

[0111] The rubber composition of the present invention can be suitably used by further comprising a filler. Examples of the fillers include, but are not limited to, a reinforcing filler, a non-reinforcing filler, and the like, and a reinforcing filler is preferred.

Examples of the reinforcing filler may include a carbon black such as furnace black, acetylene black, thermal black, channel black, and graphite; a silica such as a wet silica, a dry silica, a colloidal silica; and the like. Examples of the non-reinforcing filler include quartz powder, diatomaceous earth, zinc white, a basic magnesium carbonate, an activated calcium carbonate, a magnesium silicate, an aluminum silicate, a titanium dioxide, talc, an aluminum sulfate, a calcium sulfate, a barium sulfate, and the like.

[0112] These fillers may be used alone or in combination of two or more thereof, and the compounding amount thereof is appropriately selected within a range not impairing the effect of the present invention, and is usually in the range of 1 to 200 parts by weight, preferably in the range of 10 to 150 parts by weight, and more preferably in the range of 20 to 100 parts by weight, with respect to

100 parts by weight of rubber ingredient containing acrylic rubber.

[0113] The rubber composition of the present invention can be suitably used by further comprising a silane coupling agent. Examples of the silane coupling agent which can be used include, but are not limited to, 3-methacryloxypropyltrimethoxysilane, bis(3-(triethoxysilyl)propyl)disulfide, bis(3-triethoxysilylpropyl)trisulfide, bis(3-(triethoxysilyl)propyl) tetrasulfide, γ -mercaptopropyltriethoxysilane, 3-[ethoxybis(3,6,9,12,15-pentaoxaoctacosano-1-yloxy)silyl]-1-propanethiol, 3-octanoylthio-1-propyl-triethoxysilane, 3-trimethoxysilylpropyl-N,N-dimethylthiocarbamoyl tetrasulfide, γ -trimethoxysilylpropyl benzothiazyl tetrasulfide, 3-trimethoxysilylpropyl benzothiazole tetrasulfide, 3-thiocyanatopropyltriethoxysilane, vinyltriethoxysilane, N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane, 3-trimethoxysilylpropyl methacrylate monosulfide, γ -glycidoxypropyltriethoxysilane, 3-nitropropyltrimethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-chloropropyltrimethoxysilane, and the like.

These silane coupling agents may be used alone or in combination of two or more thereof, and the compounding amount thereof is appropriately selected depending on the intended use, and is usually in the range of 0.01 to 10 parts by weight, preferably in the range of 0.1 to 5 parts by weight, and more preferably in the range of 0.5 to 3 parts by weight, with respect to 100 parts by weight of rubber ingredient containing acrylic rubber.

[0114] The rubber composition of the present invention may include other compounding agents other than the above cross-linking agent, cross-linking accelerator, scorch retarder, filler and silane coupling agent. Examples of the other compounding agent include a dispersant such as a higher fatty acid and metal amine salt thereof, a plasticizer such

as a phthalic acid derivative, an adipic acid derivative, a sebacic acid derivative, a softener such as lubricating oil, process oil, coal tar, castor oil, calcium stearate, an antioxidant, a light stabilizer, a processing aid, an adhesive, a lubricant, a flame retardant, an anti-mold agent, an antistatic agent, a colorant, a cross-linking retarder, a resin such as polyolefin resin, polystyrene resin, polyacrylic resin, polyphenylene ether resin, polyester resin, polycarbonate resin, polyamide resin, vinyl chloride resin, fluororesin, and the like. These other compounding agents may be used alone or in combination of two or more thereof, and the compounding amount thereof is appropriately selected within a range not impairing the effectiveness of the present invention.

[0115] As a method for compounding a rubber composition of the present invention, a means conventionally utilized in the polymer processing field, for example, an open roll, a Banbury mixer, various kneaders, and the like can be used.

[0116] Examples of a method for compounding thereof include an ordinary procedure performed in the field of polymer processing can be applied. For example, it is preferable to sufficiently mix an ingredient which is difficult to decompose by heat or a reaction, and then mix a component which is easily decomposed by heat or a reaction, such as a cross-linking agent, in a short period at a temperature at which a reaction or decomposition does not occur.

[0117] [Cross-linked rubber]

The cross-linked rubber of the present invention is obtained by cross-linking the above rubber composition.

The cross-linked rubber of the present invention can be produced with the rubber composition of the present invention, by performing molding by using a molding machine corresponding to a desired shape, for example, an extruder, an injection molding machine, a

compressor, and a roll, and then performing a cross-linking reaction by heating to fix the shape as a cross-linked rubber. In this case, the rubber composition may be preliminarily shaped and then cross-linked, or may be shaped and cross-linked at the same time. The molding temperature is usually from 10 to 200 °C, preferably from 25 to 150 °C. The cross-linking temperature is usually from 100 to 250 °C, preferably from 130 to 220 °C, more preferably from 150 to 200 °C, and the cross-linking time is usually from 0.1 minutes to 10 hours, preferably from 1 minute to 5 hours. The heating method may be appropriately selected from methods used in cross-linking of rubber, such as press heating, steam heating, oven heating, and hot air heating.

[0118] The cross-linked rubber of the present invention may be further heated to perform secondary cross-linking depending on the shape, size, and the like of the cross-linked rubber. The secondary cross-linking is performed preferably for 1 to 48 hours, although the time varies according to the heating method, the cross-linking temperature, and the shape of the product. The heating method and temperature may be appropriately selected.

[0119] The cross-linked rubber of the present invention is one that has excellent compression set resistance and water resistance while maintaining basic properties of rubber such as tensile strength, elongation, and hardness. The compression set ratio measured according to JIS K6262 of the cross-linked product of the present invention is appropriately selected depending on the intended use, but is usually in the range of 1 to 50 %, preferably in the range of 5 to 25 %, and more preferably in the range of 8 to 20 %.

[0120] Taking advantage of the above properties, the cross-linked rubber of the present invention can be suitably used for, for example, a sealing material such as an O-ring, a packing, a diaphragm, an oil seal, a shaft seal, a bearing seal, a mechanical seal, a well head seal, an

electric/electronic device seal, an air compression device seal; various gaskets such as a rocker cover gasket that is attached to a connection between a cylinder block and a cylinder head, an oil pan gasket that is attached to the connection between an oil pan and a cylinder head or a transmission case, a gasket for fuel cell separator mounted between a pair of housings sandwiching a unit cell including a positive electrode, an electrolyte plate and a negative electrode, a gasket for top cover of hard disk drive; a cushioning material and an anti-vibration material; a wire coating material; an industrial belt; a tubes and a hose; a sheet; and the like.

[0121] The cross-linked rubber of the present invention is also suitably used as an extrusion molded product and a cross-linked product used in an automotive application, for example, various hoses including a fuel hose around a fuel tank such as a fuel hose, a filler neck hose, a vent hose, a paper hose, and an oil hose, an air system hose such as a turbo air hose and an emission control hose, a radiator hose, a heater hose, a brake hose, an air conditioner hose, and the like.

EXAMPLES

[0122] The present invention will now be more specifically described by way of Examples and Comparative Examples. In Examples, "parts" are expressed in terms of weight, unless otherwise specified.

A variety of physical properties were evaluated according to the following methods.

[0123] [Mooney viscosity (ML1+4, 100°C)]

The Mooney viscosity (polymer Mooney) of the acrylic rubber was measured according to JIS K6300.

[0124] [Glass transition temperature (Tg)]

The glass transition temperature (Tg) of acrylic rubber was measured according to JIS K6240.

[0125] [Mutual adhesion between hydrous crumb after washing]

15 g of a hydrous crumb after washing was placed in a cylinder having an inner diameter of 10 mm, and compressed with a 1 MPa for 30 seconds, whereby crumb particles were adhered to each other to form a cylindrical molded article. Then, the obtained cylindrical molded article was hung by sandwiching with a clip, and a time of drop was measured as a time that at least a portion of the crumb particles constituting the cylindrical molded article drops. As the time of drop is shorter, it can be determined that the mutual adhesion between hydrous crumbs after washing is lower (difficult to stick with each other). In the present Examples, the criteria were as follows.

Excellent: Time of drop is 40 seconds or less

Good: Time of drop is longer than 40 seconds and shorter than or equal to 60 seconds

Fair: Time of drop is longer than 60 seconds and shorter than or equal to 150 seconds

Poor: Time of drop is longer than 150 seconds

[0126] [Water content of acrylic rubber after drying]

The acrylic rubber after drying was placed on an aluminum tray, and then dried in an oven at 100 °C for 1 hour. The water content of the acrylic rubber after drying was determined from the weight of the acrylic rubber before and after the drying according to the following formula.

Water content of acrylic rubber after drying (wt%) = [(weight before performing a one hour-drying operation (g) - weight after performing a one hour-drying operation (g)) / weight before performing a one hour-drying operation (g)] × 100

[0127] [Recovery ratio of acrylic rubber]

The ratio of the weight of the solid acrylic rubber after coagulation and drying to the weight of the acrylic rubber in the

polymerized emulsion liquid was determined, and this was taken as the recovery ratio of acrylic rubber. The weight of the acrylic rubber in the polymerized emulsion liquid was calculated from the weight of the monomer used for the polymerization (a charged amount) and the polymerization conversion ratio. In the present Examples, the evaluation criteria were as follows.

Excellent: Recovery ratio of acrylic rubber is 100 %

Good: Recovery ratio of acrylic rubber is 95 % or more and less than 100 %

Poor: Recovery ratio of acrylic rubber is less than 95%

[0128] [Probe tack test]

For acrylic rubber composition (1), a probe tack test was performed with a tacking tester (TAC-1000 : available from RHESCA Co., LTD.). Specifically, with respect to the acrylic rubber sample molded into 30 mm × 20 mm × 2 mm, a pressing operation was performed with an SUS probe (10 mmφ) under conditions of a pressing speed of 0.05 mm/s, a pressing load of 20 gf, and a pressing holding time of 10 seconds. Then, a tack strength (N) was measured when the SUS probe was pulled up at a pulling speed of 15 mm/s. As the tack strength is lower, adhesion to a dryer and the like does not occur, resulting in good productivity (When the tack strength is high, it firmly adheres to a wall surface of a dryer or a carrier, which lowers the production efficiency. In addition, there is also a problem that uniform quality cannot be obtained, which is not preferable.). Further, the lower the tack strength is, the lower the tackiness to the roll becomes when processing it with a roll. Thus, it can be judged that it is excellent in roll processability. In the present examples, the evaluation criteria were as follows.

Excellent: Tack strength is 1.8 N or less

Good: Tack strength is greater than 1.8 N and less than or equal to 2.1 N

Fair: Tack strength is greater than 2.1 N and less than or equal to 3 N

Poor: Tack strength is greater than 3 N

[0129] [Water resistance]

Acrylic rubber composition (2) was placed in a mold having a length of 15 cm, a width of 15 cm, and a depth of 0.2 cm, and was subjected to a primary cross-linking by pressing at 170 °C for 20 minutes with applying a press pressure of 10 MPa, and then the obtained primary cross-linked product was further heated in a geared oven at 170 °C for 4 hours to perform a secondary cross-linking, so that a sheet-shaped cross-linked rubber was obtained. Then, from the obtained sheet-shaped cross-linked rubber, a test piece of 3 cm × 2 cm × 0.2 cm was cut out. According to a JIS K6258, an immersion test was performed in which the obtained test piece was immersed in distilled water adjusted to a temperature of 80 °C for 70 hours. A change ratio of volume of the test piece before and after the immersion was measured according to the following formula. It can be determined that a smaller change ratio of volume before and after the immersion indicates a smaller degree of swelling of the cross-linked rubber by water, and thus higher water resistance. In the present Examples, the criteria were as follows.

Excellent: Change ratio of volume is 19% or less

Good: Change ratio of volume is greater than 19% and less than or equal to 24%

Fair: Change ratio of volume is greater than 24% and less than or equal to 30%

Poor: Change ratio of volume is greater than 30%

Change ratio (%) of volume before and after immersion =
[(volume of test piece after immersion) - (volume of test piece before immersion)] / (volume of test piece before immersion) × 100

[0130] [Example 1]

[Polymerization of acrylic rubber]

46.294 parts of pure water, 49.3 parts of ethyl acrylate, 49.3 parts of n-butyl acrylate, 1.4 parts of mono-n-butyl fumarate, 0.567 parts of sodium lauryl sulfate as an anionic surfactant (product name "EMAL 2FG", available from Kao Corporation), and 1.4 parts of polyoxyethylene dodecyl ether as a compound having a polyoxyalkylene skeleton (product name "EMULGEN 105", weight average molecular weight (Mw) = about 1,500, available from Kao Corporation) were placed in a mixing container equipped with a homomixer, and stirred to obtain a monomer emulsion.

[0131] In the next step, 170.853 parts of pure water and 2.97 parts of the monomer emulsion prepared above were placed into a polymerization reaction tank provided with a thermometer and a stirrer, and the mixture was cooled to a temperature of 12 °C under a nitrogen stream. Then, 145.29 parts of the monomer emulsion prepared above, 0.00033 parts of ferrous sulfate as a reducing agent, 0.264 parts of sodium ascorbate as a reducing agent, and 7.72 parts of a 2.85 wt% aqueous solution of potassium persulfate (0.22 parts in terms of potassium persulfate) as a polymerization initiator were continuously added dropwise into the polymerization reaction tank over three hours. Subsequently, the reaction was continued for one hour in the state where the inner temperature of the polymerization reaction tank was kept at 23 °C. After it was checked that the polymerization conversion ratio reached 95 %, hydroquinone as a polymerization terminator was added to terminate the polymerization reaction. A polymerized emulsion liquid was thereby prepared.

[0132] [Coagulation and isolation of acrylic rubber].

Then, with respect to 100 parts of the polymerized emulsion liquid obtained by polymerization, 0.3 parts of stearyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (product name "Irganox 1076", available

from BASF SE) as an antioxidant, 0.011 parts of polyethylene oxide (weight average molecular weight (M_w) = 100,000, the weight average molecular weight was measured with GPC using a 10 mmol LiBr-containing DMF solvent) as a compound having a polyoxyalkylene skeleton (polyalkylene glycol (A)), and 0.075 parts of polyoxyethylene stearyl ether phosphate (product name "Phosphanol RL-210", weight average molecular weight (M_w) = about 500, available from Toho Chemical Industry Co., Ltd.) as compound having a polyoxyalkylene skeleton (an ester of a polyalkylene glycolester (B1)) was mixed to obtain a mixed liquid. 0.3 parts of stearyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate is equal to 1 part of the same with respect to 100 parts of total of charged monomers used when producing the polymerized emulsion liquid (that is, the total of ethyl acrylate, n-butyl acrylate, and mono-n-butyl fumarate). 0.011 parts of polyethylene oxide is equal to 0.039 parts of the same with respect to 100 parts of the total amount of the monomers charged when producing the polymerized emulsion liquid. 0.075 parts of polyoxyethylene stearyl ether phosphate is equal to 0.25 parts of the same with respect to 100 parts of the total amount of charged monomers used when producing the polymerized emulsion liquid. Then, the obtained mixed liquid was transferred to a coagulation tank, and 60 parts of industrial water was added to 100 parts of the mixed liquid. The temperature was increased to 85 ° C, and then, 3.3 parts of sodium sulfate as a coagulant (11 parts with respect to 100 parts of the polymer contained in the mixed liquid) was continuously added while stirring the mixed liquid at a temperature of 85 °C. The polymer was coagulated and then filtered separately to obtain hydrous crumbs of acrylic rubber (A1).

[0133] [Washing and drying of acrylic rubber]

In the next step, 388 parts of industrial water was added with respect to 100 parts (on a solids content basis) of the obtained

hydrous crumbs, followed by stirring at room temperature for 5 minutes in the coagulation tank. Water was then discharged from the coagulation tank to complete washing of the hydrous crumbs with water. Such an operation to wash hydrous crumbs with water was repeated 4 times in the present Example.

[0134] Then, an aqueous sulfuric acid solution (pH=3) obtained by mixing 388 parts of industrial water and 0.13 parts of concentrated sulfuric acid was added to 100 parts of solid content of the hydrous crumb subjected to water washing above, and the mixture was stirred in a coagulation tank at room temperature for 5 minutes, followed by acid washing of the hydrous crumbs by discharging water from the coagulation tank. The measurement of the pH of the hydrous crumbs after acid washing (pH of water in the hydrous crumbs) showed that pH = 3. Next, 388 parts of pure water was added to 100 parts of the solid content of the hydrous crumbs subjected to the acid washing, and the mixture was stirred at room temperature for 5 minutes. Then, the water was discharged from the coagulation tank to wash the hydrous crumbs with pure water. Then, for the hydrous crumbs after washing, mutual adhesion property of the hydrous crumbs after washing was measured according to the above method. The results are shown in Table 1.

[0135] Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (A1), and the water content of the polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0136] [Characterization of acrylic rubber]

The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A1) was 33, and the glass transition temperature (T_g) of the acrylic rubber (A1) was -30 °C. The composition of the acrylic rubber (A1) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

[0137] [Production of acrylic rubber composition (1)]

Using a Banbury mixer, to 100 parts of the acrylic rubber (A1) obtained above, 60 parts of carbon black (product name "Seast SO", available from TOKAI CARBON CO., LTD.), 2 parts of stearic acid, and 2 parts of 4,4'-bis(α,α -dimethylbenzyl) diphenylamine (product name "Nocrac CD", available from OUCHI SHINKO CHEMICAL INDUSTRIAL Co., Ltd.) were added and mixed at 50 °C for 5 minutes. Then, the obtained mixture was transferred to a roll at 50 °C, and 0.6 parts of hexamethylenediamine carbamate (product name "Diak#1", available from DuPont Dow Elastomer Co., Ltd., an aliphatic polyvalent amine compound) and 2 parts of 1,3-di-o-tolylguanidine (product name "Nocceler DT", available from OUCHI SHINKO CHEMICAL INDUSTRIAL Co., Ltd., a cross-linking accelerator) were compounded and kneaded to obtain an acrylic rubber composition (1). Then, a probe tack test was performed by using the obtained acrylic rubber composition (1) according to the above method. The results are shown in Table 1.

[0138] [Production of Acrylic rubber composition (2)]

Using a Banbury mixer, to 100 parts of the acrylic rubber (A1), 30 parts of clay (product name "Satinton Clay 5A", available from Takehara Chemical Industry Co., Ltd., calcined kaolin), 15 parts of silica (product name "Carplex 1120", available from Evonik A.G.), 35 parts of silica (product name "Carplex 67", available from Evonik A.G.), 2 parts of stearic acid, 1 part of ester-based wax (product name "GLECK G-8205", available from DIC Corporation), 2 parts of 4,4'-bis(α,α -dimethylbenzyl)diphenylamine (product name "Nocrac CD", available from OUCHI SHINKO CHEMICAL INDUSTRIAL Co., Ltd.), and 1 part of 3-methacryloxypropyltrimethoxysilane (product name "KBM-503", available from Shin-Etsu Silicone Co., Ltd., a silane coupling agent) were added and mixed at 50 °C for 5 minutes. Then, the obtained mixture was transferred to a roll at 50 °C, and 0.6 parts of hexamethylenediamine

carbamate (product name "Diak#1", available from DuPont Dow Elastomer Co., Ltd., an aliphatic polyvalent amine compound) and 2 parts of 1,3-di-o-tolylguanidine (product name "Nocceler DT", available from OUCHI SHINKO CHEMICAL INDUSTRIAL Co., Ltd., a cross-linking accelerator) were compounded and kneaded to obtain an acrylic rubber composition (2). Then, the obtained acrylic rubber composition (2) was used to evaluate the water resistance according to the above method. The results are shown in Table 1.

[0139] [Example 2]

A monomer emulsion was obtained in the same manner as Example 1, except that 1.4 parts of polyoxyethylene monostearic acid ester (product name "Nonion S40", weight-average molecular weight (Mw) = about 4,800, available from NOF Corporation) was used instead of polyoxyethylene dodecyl ether as a compound having a polyoxyalkylene skeleton to be composed in preparing a monomer emulsion. Then, using the obtained monomer emulsion, emulsion polymerization was carried out in the same manner as Example 1 to obtain a polymerized emulsion liquid.

[0140] Then, using the polymerized emulsion liquid obtained above, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Example 1, hydrous crumbs of the acrylic rubber (A2) were obtained. Further, 4 times of washing with water, acid washing, and washing with pure water were performed on the obtained hydrous crumbs of the acrylic rubber (A2) in the same manner as Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumbs after washing was measured according to the above method. The results are shown in Table 1.

[0141] Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (A2), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A2) was 33, and the glass transition temperature (T_g) of the acrylic rubber (A2) was -30 °C. The composition of the acrylic rubber (A2) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

[0142] An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that the acrylic rubber (A2) was used instead of the acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0143] [Example 3]

A monomer emulsion was obtained in the same manner as Example 1, except that 1.4 parts of polyoxyethylene nonylphenyl ether (product name "NOIGEN EA70", weight-average molecular weight (M_w) = 600, available from DKS Co. Ltd.) was used instead of polyoxyethylene dodecyl ether as a compound having a polyoxyalkylene skeleton to be compounded in preparing a monomer emulsion. Then, using the obtained monomer emulsion, emulsion polymerization was carried out in the same manner as Example 1 to obtain a polymerized emulsion liquid.

[0144] Then, using the polymerized emulsion liquid obtained above, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Example 1, hydrous crumbs of acrylic rubber (A3) was obtained. Further, 4 times of washing with water, acid washing, and washing with pure water were performed on the obtained hydrous crumbs of the acrylic rubber (A3) in the same manner as Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of the hydrous crumbs after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing were dried in a hot air dryer at 110 °C for 1 hour to obtain the solid acrylic rubber (A3),

and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0145] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A3) was 33, the glass transition temperature (T_g) of the acrylic rubber (A3) was -30 °C. The composition of the acrylic rubber (A3) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that the acrylic rubber (A3) was used instead of the acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0146] [Example 4]

A monomer emulsion was obtained in the same manner as Example 1, except that polyoxyethylene dodecyl ether as a compound having a polyoxyalkylene skeleton was not compounded. Then, using the monomer emulsion obtained above, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Example 1, hydrous crumbs of acrylic rubber (A4) was obtained, except that the amount of polyethylene oxide added as a compound having a polyoxyalkylene skeleton was changed from 0.011 parts to 0.09 parts with respect to 100 parts by weight of the obtained polymerized emulsion liquid (0.3 parts with respect to 100 parts of the total amount of charged monomers used when producing the polymerized emulsion liquid).

Then, the hydrous crumbs of the obtained acrylic rubber (A4) was subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumbs after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 ° C for 1 hours to obtain a solid acrylic rubber (A4), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0147] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A4) was 33, the glass transition temperature (T_g) of the acrylic rubber (A4) was -30 °C. The composition of the acrylic rubber (A4) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that the acrylic rubber (A4) was used instead of the acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0148] [Example 5]

Using the polymerized emulsion liquid obtained in the same manner as Example 4, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Example 4, hydrous crumbs of acrylic rubber (A5) was obtained, except that the amount of polyethylene oxide added as a compound having a polyoxyalkylene skeleton was changed from 0.011 parts to 0.42 parts with respect to 100 parts by weight of the obtained polymerized emulsion liquid (1.4 parts with respect to 100 parts of the total amount of charged monomers used when producing the polymerized emulsion liquid).

Then, the hydrous crumbs of the obtained acrylic rubber (A5) were subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as in Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumb after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (A5), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0149] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A5) was 33, the glass transition temperature (T_g) of the acrylic rubber (A5) was -30 °C. The composition of the acrylic rubber (A5) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that the acrylic rubber (A5) was used instead of acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0150] [Example 6]

A mixed liquid was obtained in the same manner as Example 1 by using a polymerized emulsion liquid obtained in the same manner as Example 1, except that polyethylene oxide as a compound having a polyoxyalkylene skeleton was not compounded. Then, a coagulation operation was performed in the same manner as in Example 1, except that the amount of sodium sulfate used as coagulant was changed from 3.3 parts to 7 parts (23.3 parts with respect to 100 parts of the polymer contained in the mixed liquid), thereby obtaining hydrous crumbs of the obtained acrylic rubber (A6).

Then, the hydrous crumbs of the obtained acrylic rubber (A6) was subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumb after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (A6), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0151] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A6) was 33, the glass transition temperature (T_g) of the acrylic rubber (A6) was -30 °C. The composition of the acrylic rubber (A6) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that the acrylic rubber (A6) was used instead of the acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0152] [Example 7]

Using a polymerized emulsion liquid obtained in the same manner as Example 1, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Example 1, hydrous crumbs of acrylic rubber (A7) was obtained, except that the amount of polyethylene oxide added as a compound having a polyoxyalkylene skeleton was changed from 0.011 parts to 0.42 parts with respect to 100 parts by weight of the obtained polymerized emulsion liquid in the same manner as Example 1 (1.4 parts with respect to 100 parts of the total amount of charged monomers used when producing the polymerized emulsion liquid), and polyoxyethylene stearyl ether phosphate as a compound having a polyoxyalkylene skeleton was not compounded.

Then, the hydrous crumbs of the obtained acrylic rubber (A7) was subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumb

after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (A7), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0153] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A7) was 33, the glass transition temperature (T_g) of the acrylic rubber (A7) was -30 °C. The composition of the acrylic rubber (A7) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that the acrylic rubber (A7) was used instead of the acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0154] [Example 8]

Using the polymerized emulsion liquid obtained in the same manner as Example 1, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Example 1, hydrous crumbs of acrylic rubber (A8) was obtained, except that polyoxyethylene stearyl ether phosphate as a compound having a polyoxyalkylene skeleton was not compounded.

Then, the hydrous crumbs of the obtained acrylic rubber (A8) was subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as in Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumb after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air

dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (A8), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0155] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A8) was 33, the glass transition temperature (T_g) of the acrylic rubber (A8) was -30 °C. The composition of the acrylic rubber (A8) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that acrylic rubber (A8) was used instead of acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0156] [Comparative Example 1]

A monomer emulsion was obtained in the same manner as Example 1, except that polyoxyethylene dodecyl ether as a compound having a polyoxyalkylene skeleton was not compounded. Then, in the same manner as Example 1, except that the obtained monomer emulsion was used, the preparation of the mixed liquid and coagulation operation were performed to obtain hydrous crumbs of acrylic rubber (C1).

Then, the hydrous crumbs of the obtained acrylic rubber (C1) was subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumb after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (C1), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0157] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (C1) was 33, the glass transition temperature (Tg) of the acrylic rubber (C1) was -30 °C. The composition of the acrylic rubber (C1) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that acrylic rubber (C1) was used instead of acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0158] [Comparative Example 2]

Using a polymerized emulsion liquid obtained in the same manner as Comparative Example 1, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Comparative Example 1, hydrous crumbs of acrylic rubber (C2) was obtained, except that the amount of polyethylene oxide added as a compound having a polyoxyalkylene skeleton was changed from 0.011 parts to 1.2 parts with respect to 100 parts by weight of the obtained polymerized emulsion liquid in the same manner as Comparative Example 1 (4 parts with respect to 100 parts of the total amount of charged monomers used when producing the polymerized emulsion liquid), and polyoxyethylene stearyl ether phosphate as a compound having a polyoxyalkylene skeleton was not compounded.

Then, the hydrous crumbs of the obtained acrylic rubber (C2) was subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumb after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air

dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (C2), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0159] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (C2) was 33, the glass transition temperature (T_g) of the acrylic rubber (C2) was -30 °C. The composition of the acrylic rubber (C2) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as in Example 1, except that acrylic rubber (C2) was used instead of acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0160] [Comparative Example 3]

Using a polymerized emulsion liquid obtained in the same manner as Example 4, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Example 4, hydrous crumbs of acrylic rubber (C3) was obtained, except that polyethylene oxide as a compound having a polyoxyalkylene skeleton was not compounded.

Then, the hydrous crumbs of the obtained acrylic rubber (C3) was subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as in Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumb after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (C3), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0161] The Mooney viscosity (ML1+4, 100 °C.) of the obtained acrylic rubber (C3) was 33, the glass transition temperature (T_g) of the acrylic rubber (C3) was -30 °C. The composition of the acrylic rubber (C3) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that acrylic rubber (C3) was used instead of acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0162] [Comparative Example 4]

Using a polymerized emulsion liquid obtained in the same manner as Example 1, by performing the preparation of the mixed liquid and coagulation operation in the same manner as Example 1, hydrous crumbs of acrylic rubber (C4) was obtained, except that polyethylene oxide as a compound having a polyoxyalkylene skeleton and polyoxyethylene stearyl ether phosphate as a compound having a polyoxyalkylene skeleton were not compounded.

Then, the hydrous crumbs of the obtained acrylic rubber (C4) was subjected to 4 times of washing with water, acid washing, and washing with pure water in the same manner as Example 1. Then, for the hydrous crumbs after washing, mutual adhesion property of hydrous crumb after washing was measured according to the above method. The results are shown in Table 1.

Then, the hydrous crumbs after washing was dried in a hot air dryer at 110 °C for 1 hour to obtain a solid acrylic rubber (C4), and the water content of polymer and the recovery ratio of the acrylic rubber were measured. The results are shown in Table 1.

[0163] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (C4) was 33, the glass transition temperature (T_g) of the acrylic

rubber (C4) was -30 °C. The composition of the acrylic rubber (C4) was 49.3 wt% of ethyl acrylate units, 49.3 wt% of n-butyl acrylate units, and 1.4 wt% of mono-n-butyl fumarate units.

An acrylic rubber composition (1) and an acrylic rubber composition (2) were obtained in the same manner as Example 1, except that acrylic rubber (C4) was used instead of acrylic rubber (A1) in Example 1, and measurement and evaluation were similarly performed. The results thereof are shown in Table 1.

[0164]

[Table 1]

Table 1

		unit	Example								Comparative Example			
			1	2	3	4	5	6	7	8	1	2	3	4
Type of acrylic rubber			(A1)	(A2)	(A3)	(A4)	(A5)	(A6)	(A7)	(A8)	(C1)	(C2)	(C3)	(C4)
Monomer composition (*1)	Ethyl acrylate	(parts)	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3
	n-Butyl acrylate	(parts)	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3	49.3
	Mono-n-butyl fumarate	(parts)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Anionic emulsifier	Sodium lauryl sulfate (anionic emulsifier)	(parts)	0.567	0.567	0.567	0.567	0.567	0.567	0.567	0.567	0.567	0.567	0.567	0.567
Nonionic emulsifier	Polyoxyethylene dodecyl ether (compound having polyoxyalkylene skeleton)	(parts)	1.4					1.4	1.4	1.4				1.4
	Polyoxyethylene monostearate (compound having polyoxyalkylene skeleton)	(parts)		1.4										
	Polyoxyethylene nonyl phenyl ether (compound having polyoxyalkylene skeleton)	(parts)			1.4									
	Polyethylene oxide (compound having polyoxyalkylene skeleton)	(parts)	0.011	0.011	0.011	0.09	0.42		0.42	0.011	0.011	1.2		
Polyethylene oxide skeleton compound (*2)	Polyoxyethylene stearyl ether phosphate (compound having polyoxyalkylene skeleton)	(parts)	0.075	0.075	0.075	0.075	0.075	0.075					0.075	
Coagulant used in the coagulation step (*3)	Sodium sulfate	(parts)	3.3	3.3	3.3	3.3	3.3	7	3.3	3.3	3.3	3.3	3.3	3.3
Washing with water	Times of washing with water	(times)	4	4	4	4	4	4	4	4	4	4	4	4
Hydrous crumb after washing	Mutual adhesion hydrous crumb after washing (time of drop)	(sec)	Excellent	Excellent	Good	Good	Excellent	Excellent	Excellent	Excellent	Poor	Good	Poor	Excellent
Recovery ratio	Recovery ratio of acrylic rubber	(%)	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Excellent	Excellent	Excellent	Excellent	Poor	Poor
Evaluation	Water content of polymer after drying	(%)	0	0	0	0.4	0	0	0	0	2.7	0	2.6	0
	Tack strength (probe tack test)	(N)	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Good	Fair	Poor	Fair	Good	Poor
	Volume change ratio after immersion in water (water resistance)	(%)	Excellent	Excellent	Excellent	Good	Good	Fair	Good	Excellent	Excellent	Poor	Excellent	Excellent

[0165] From Table 1, the acrylic rubber of the present invention obtained by coagulating the polymerized emulsion liquid in the presence of two or more types of compounds having a polyoxyalkylene skeleton prevents the mutual adhesion between hydrous crumbs, and excellent in the polymer recovery ratio and drying properties. Further, it is understood that the rubber composition obtained by using the acrylic rubber of the present invention has low tack strength in the probe tack test, and is excellent in productivity in a dryer and roll processability. In addition, it can be seen that the cross-linked rubber obtained by using the acrylic rubber is excellent in water resistance, and excellent in any of the five properties (Examples 1 to 8).

[0166] On the other hand, when coagulation is performed using only one kind of polyethylene oxides as a polymer compound having a polyoxyalkylene skeleton, it can be seen that the obtained acrylic rubber provides hydrous crumbs with poor mutual adhesion and drying properties, as well as excessive high tack strength, resulting in inferior productivity and roll processability (Comparative Example 1). It can be seen that, when the amount of polyethylene oxide used in Comparative Example 1 is increased, mutual adhesion property, the drying property and the tackiness of hydrous crumb are improved, but there is a problem that the water resistance is extremely deteriorated (Comparative Example 2). Moreover, when coagulation is carried out using only one type of low molecular weight compound having a polyoxyalkylene skeleton, it turns out that there is a problem that not only the mutual adhesion and drying properties of the hydrous crumbs are poor but also the recovery ratio of the polymer is low (Comparative Example 3). On the other hand, there is a problem that not only the tackiness is extremely poor but also the polymer recovery is low (Comparative Example 4). From these comparative examples, it can be seen that it is difficult to balance the 5 properties of mutual adhesion property of hydrous crumbs,

the recovery ratio of polymer, the drying property, and the tack property and the water resistance of a rubber composition and a cross-linked rubber (Comparative Examples 1 to 4). In other words, although any of the characteristics of the Comparative Examples was extremely deteriorated (Comparative Examples 1 to 4), it was found that the acrylic rubber obtained by the production method of the present invention is a well-balanced result in which none of the 5 characteristics is extremely poor (Examples 1 to 8).

CLAIMS

1. A method for producing an acrylic rubber, comprising:
an emulsion polymerization step of emulsion polymerizing a monomer for forming the acrylic rubber so as to obtain a polymerized emulsion liquid; and
a coagulation step of coagulating the polymerized emulsion liquid in the presence of two or more types of compounds having a polyoxyalkylene skeleton so as to obtain a hydrous crumb.
2. The method for producing the acrylic rubber according to claim 1, further comprising an emulsion preparation step of obtaining a monomer emulsion by mixing the monomer for forming the acrylic rubber with an emulsifier and water prior to the emulsion polymerization step, and
wherein the compounds having the polyoxyalkylene skeleton are added in a manner of mixing the compounds with the monomer emulsion obtained in the emulsion preparation step and/or mixing the compounds with the polymerized emulsion liquid obtained in the emulsion polymerization step.
3. The method for producing the acrylic rubber according to claim 1 or 2, wherein at least one type of compound selected from the group consisting of a homopolymer of oxyalkylene, a copolymer of two or more oxyalkylenes, a polyoxyalkylene alkyl ether, a polyoxyalkylene aryl ether, a polyoxyalkylene alkyl ester, and a polyoxyalkylene alkyl ether ester is used as the compounds having the polyoxyalkylene skeleton.
4. The method for producing the acrylic rubber according to any one of claims 1 to 3, wherein at least two types of compounds, which are

different from each other, selected from the group consisting of a homopolymer of oxyalkylene, a copolymer of two or more oxyalkylenes, a polyoxyalkylene alkyl ether, a polyoxyalkylene aryl ether, a polyoxyalkylene alkyl ester, and a polyoxyalkylene alkyl ether ester are used as the compounds having the polyoxyalkylene skeleton.

5. The method for producing the acrylic rubber according to any one of claims 1 to 4, wherein the coagulation step is a step of obtaining the hydrous crumb by coagulating the polymerized emulsion liquid in the presence of two or more types of compounds having the polyoxyalkylene skeleton, the compounds having different molecular weights.

6. The method for producing the acrylic rubber according to claim 5, wherein a low molecular weight compound ($\alpha 1$) having a polyoxyalkylene skeleton and a weight average molecular weight (Mw) of less than 10,000; and a high molecular weight compound ($\alpha 2$) having a polyoxyalkylene skeleton and a weight average molecular weight (Mw) of 10,000 or more are used as the compounds having the polyoxyalkylene skeleton.

7. The method for producing the acrylic rubber according to claim 6, wherein the weight average molecular weight (Mw) of the low molecular weight compound ($\alpha 1$) is in the range of 100 to 8,000, and the weight average molecular weight (Mw) of the high molecular weight compound ($\alpha 2$) is in the range of 20,000 to 6,000,000.

8. The method for producing the acrylic rubber according to any one of claims 1 to 7, wherein the coagulating step is a step of obtaining the hydrous crumb by coagulating the polymerized emulsion

liquid in the presence of polyalkylene glycol (A) and an ester compound of a polyalkylene glycol (B1) and/or an ether compound of a polyalkylene glycol (B2).

9. The method for producing the acrylic rubber according to claim 8, wherein the polyalkylene glycol (A) is added to the polymerized emulsion liquid after emulsion polymerization.

10. The method for producing the acrylic rubber according to claim 8 or 9, further comprising an emulsion preparation step of obtaining a monomer emulsion by mixing the monomer for forming the acrylic rubber with an emulsifier and water prior to the emulsion polymerization step, and

wherein the ester compound of the polyalkylene glycol (B1) and/or the ether compound of the polyalkylene glycol (B2) are added to the monomer emulsion before emulsion polymerization and/or the polymerized emulsion liquid after emulsion polymerization.

11. The method for producing the acrylic rubber according to any one of claims 8 to 10, wherein the ester compound of the polyalkylene glycol (B1) and/or the ether compound of the polyalkylene glycol (B2) are at least one of polyoxyalkylene ester compound selected from the group consisting of polyoxyalkylene phosphoric ester, polyoxyalkylene sulfate ester, polyoxyalkylene fatty acid ester, and polyoxyalkylene ether ester and/or at least one polyoxyalkylene ether compound having no ester group selected from the group consisting of polyoxyalkylene alkyl ether and polyoxyalkylene aryl ether.

12. The method for producing the acrylic rubber according to any one of claims 1 to 11, wherein the monomer for forming the acrylic

rubber contains 30 wt% or more of a (meth)acrylic ester monomer.

13. The method for producing the acrylic rubber according to claim 12, wherein the monomer for forming the acrylic rubber contains 30 wt% or more of a (meth)acrylic acid alkyl ester monomer and/or a (meth)acrylic acid alkoxyalkyl ester monomer, both ester monomers having an alkyl group with two or more carbon atoms.

14. The method for producing the acrylic rubber according to any one of claims 1 to 13, wherein the monomer for forming the acrylic rubber contains a cross-linkable monomer.

15. The method for producing the acrylic rubber according to claim 14, wherein the monomer for forming the acrylic rubber contains 0.01 wt% or more of the cross-linkable monomer.

16. The method for producing the acrylic rubber according to claim 14 or 15, wherein the cross-linkable monomer is at least one monomer selected from the group consisting of a carboxyl group-containing monomer, an epoxy group-containing monomer, a halogen group-containing monomer, and a diene monomer.

17. The method for producing the acrylic rubber according to any one of claims 14 to 16, wherein the monomer for forming the acrylic rubber contains 50 to 99.9 wt% of a (meth)acrylic ester monomer and 0.1 to 50 wt% of the cross-linkable monomer.

18. The method for producing the acrylic rubber according to any one of claims 1 to 17, wherein emulsion polymerization in the emulsion polymerization step is performed with using a material containing a

peroxide, ferrous sulfate, and an ascorbic acid or a salt of an ascorbic acid as a polymerization catalyst.

19. The method for producing the acrylic rubber according to any one of claims 1 to 18, wherein coagulation in the coagulation step is performed by contacting the polymerized emulsion liquid with a sulfate compound.

20. The method for producing the acrylic rubber according to claim 19, wherein coagulation in the coagulation step is performed in a manner of adding a metal sulfate to the polymerized emulsion liquid or in a manner of adding the polymerized emulsion liquid to an aqueous solution containing the metal sulfate.

21. The method for producing the acrylic rubber according to claim 20, wherein the metal sulfate is a monovalent metal sulfate.

22. The method for producing the acrylic rubber according to any one of claims 1 to 21, wherein a coagulation temperature in the coagulation step is 60 °C or more.

23. The method for producing the acrylic rubber according to any one of claims 1 to 22, comprising:

a washing step of performing washing on the hydrous crumb;

and

a drying step of drying the washed hydrous crumb.

24. The method for producing the acrylic rubber according to claim 23, wherein the washing step comprises an acid washing.

25. An acrylic rubber obtained by the method according to any one of claims 1 to 24.

26. The acrylic rubber according to claim 25, wherein a (meth)acrylate unit is from 50 to 99.9 wt%, a cross-linkable monomer unit is from 0.01 to 20 wt%, and a copolymerizable other monomer unit is from 0 to 49.99 wt%.

27. The acrylic rubber according to claim 26, wherein the cross-linkable monomer unit is a carboxyl group-containing monomer unit.

28. The acrylic rubber according to any one of claims 25 to 27, wherein a Mooney viscosity is in the range of 10 to 150.

29. The acrylic rubber according to claim 28, wherein the Mooney viscosity is in the range of 10 to 80.

30. The acrylic rubber according to any one of claims 25 to 29, wherein a glass transition temperature (T_g) is 25 °C or less.

31. A rubber composition comprising a rubber ingredient and a cross-linking agent, the rubber ingredient comprising the acrylic rubber according to any one of claims 25 to 30.

32. The rubber composition according to claim 31, further comprising a cross-linking accelerator, an antioxidant, a filler or a silane coupling agent.

33. A cross-linked rubber prepared by cross-linking the rubber composition according to claim 31 or 32.