

DESCRIPTION

METHOD FOR PRODUCING ACRYLIC RUBBER, AND ACRYLIC RUBBER OBTAINED BY SAID PRODUCTION METHOD

TECHNICAL FIELD

[0001] The present invention relates to a method for producing an acrylic rubber, an acrylic rubber obtained by the production method, a rubber composition containing the acrylic rubber, and a cross-linked rubber obtained by cross-linking the rubber composition. More particularly, the present invention relates to a method for producing an acrylic rubber excellent in storage stability, an acrylic rubber obtained by the production method, a rubber composition containing the acrylic rubber, and a cross-linked rubber obtained by cross-linking the rubber composition.

BACKGROUND ART

[0002] Acrylic rubber is a polymer containing an acrylic acid ester as a main component. Acrylic rubber is generally known as a rubber excellent in heat resistance, oil resistance and ozone resistance, and is widely used in automotive-related fields and the like.

[0003] Such an acrylic rubber is usually produced as follows. A mixture of monomers for forming the acrylic rubber is emulsion polymerized. A coagulant is then added to the resulting polymer emulsion to cause coagulation, and hydrous crumbs produced by the coagulation are dried (for example, see Patent Document 1). For drying hydrous crumbs, a drying device capable of drying in a continuous process, such as a belt conveyor type band dryer and an extruder, is used from the viewpoint of productivity. On the other hand, it has been a problem that, in the acrylic rubber thus produced, scorching, burning, and the like occur in

storage for a long period of time.

RELATED ART DOCUMENTS

PATENT DOCUMENTS

[0004] Patent Document 1: Japanese Unexamined Patent Application
Publication No. H07-145291

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0005] The present invention has been made in consideration of such circumstances. It is an object of the present invention to provide a method for producing an acrylic rubber capable of realizing excellent storage stability while keeping normal physical properties good.

MEANS FOR SOLVING THE PROBLEM

[0006] The present inventors have intensively studied to achieve the above object. As a result, it has been found that, in a method for producing an acrylic rubber, emulsion polymerization is performed by combining particular two emulsifiers, the obtained polymerized emulsion liquid is coagulated using a metallic sulfate, and the obtained hydrous crumb is washed and dried, whereby an acrylic rubber capable of realizing excellent storage stability while keeping normal physical properties good can be produced.

[0007] In addition, the present inventors have found that the object of the present invention can be further highly achieved by employing at least one of the following aspects: the acrylic rubber comprises a cross-linkable functional group, using two emulsifiers in a specific ratio and using a redox-based polymerization catalyst as a polymerization initiator, in particular combining particular two reducing agents, using a monovalent or divalent metal sulfate as a

coagulant, and contacting a polymerized emulsion liquid with a metal sulfate while being warmed and performing washing comprising acid washing. Thus, the present inventors have accomplished the present invention.

[0008] Accordingly, the present invention provides a method for producing an acrylic rubber comprising: an emulsion polymerization step of emulsion polymerizing a monomer comprising a (meth)acrylic acid ester and at least one cross-linkable monomer selected from the group consisting of a carboxyl group-containing monomer, an epoxy group-containing monomer and a halogen group-containing monomer in the presence of a nonionic emulsifier and an anionic emulsifier with a polymerization initiator to obtain a polymerized emulsion liquid; a coagulation step of coagulating the polymerized emulsion liquid by contacting with a metal sulfate to obtain a hydrous crumb; a washing step of performing washing on the hydrous crumb; and a drying step of drying the hydrous crumb that is washed.

In the method for producing the acrylic rubber of the present invention, it is preferable that the use ratio of the nonionic emulsifier and the anionic emulsifier is in the range of 1/99 to 99/1 in terms of a weight ratio of the nonionic emulsifier/the anionic emulsifier.

In the method for producing the acrylic rubber of the present invention, it is preferable that the use ratio of the nonionic emulsifier and the anionic emulsifier is in the range of 50/50 to 75/25 in terms of a weight ratio of the nonionic emulsifier/the anionic emulsifier.

[0009] In the method for producing the acrylic rubber of the present invention, it is preferable that the polymerization initiator is used in combination with a reducing agent.

In the method for producing the acrylic rubber of the present

invention, it is preferable that at least two compounds are used as the reducing agent.

In the method for producing the acrylic rubber of the present invention, it is preferable that the metal ion-containing compound in a reduced state and a reducing agent other than the metal ion-containing compound in the reduced state are used in combination as the reducing agent.

In the method for producing the acrylic rubber of the present invention, it is preferable that the metal ion-containing compound in the reduced state is ferrous sulfate.

In the method for producing the acrylic rubber of the present invention, it is preferable that the reducing agent other than the metal ion-containing compound in the reduced state is sodium formaldehyde sulfoxylate, ascorbic acid or ascorbate.

In the method for producing the acrylic rubber of the present invention, it is preferable that the reducing agent other than the metal ion-containing compound in the reduced state is ascorbate.

[0010] In the method for producing the acrylic rubber of the present invention, it is preferable that the polymerization initiator is an organic peroxide or an inorganic peroxide.

In the method for producing the acrylic rubber of the present invention, it is preferable that contacting the polymerized emulsion liquid with the metal sulfate is carried out in a manner of adding the metal sulfate to the polymerized emulsion liquid or in a manner of adding the polymerized emulsion liquid into a solution of the metal sulfate or a dispersion of the metal sulfate.

In the method for producing the acrylic rubber of the present invention, it is preferable that a contacting temperature of the polymerized emulsion liquid and the metal sulfate is 60 °C or higher.

In the method for producing the acrylic rubber of the present

invention, it is preferable that the metal sulfate is a monovalent or divalent metal sulfate.

In the method for producing the acrylic rubber of the present invention, it is preferable that the anionic emulsifier is a phosphate ester salt.

In the method for producing the acrylic rubber of the present invention, it is preferable that the washing comprises acid washing.

[0011] Further, the present invention provides an acrylic rubber produced by the method as mentioned above.

In the acrylic rubber of the present invention, it is preferable that a monomer composition is 50 to 99.9 wt% of (meth)acrylic acid ester monomer units, 0.01 to 20 wt% of cross-linkable monomer units, and 0 to 49.99 wt% of other copolymerizable monomer units.

In the acrylic rubber of the present invention, it is preferable that a Mooney viscosity (ML1+4, 100 °C) is in the range of 10 to 150.

[0012] Further, the present invention provides a rubber composition comprising a rubber ingredient and a cross-linking agent, the rubber ingredient comprising the acrylic rubber as mentioned above.

In the rubber composition of the present invention, it is preferable that the cross-linking agent is at least one selected from the group consisting of a polyvalent amine compound, a polyvalent epoxy compound, a polyvalent carboxylic acid, an organic carboxylic acid ammonium salt, an organic carboxylic acid metal salt, an isocyanuric acid compound, a triazine compound, and a metal soap/sulfur.

In the rubber composition of the present invention, it is preferable that the rubber composition further comprises a cross-linking accelerator.

In the rubber composition of the present invention, it is preferable that the cross-linking accelerator is at least one selected

from the group consisting of 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 vulcanizing accelerator.

In the rubber composition of the present invention, it is preferable that the rubber composition further comprises a scorch inhibitor.

In the rubber composition of the present invention, it is preferable that the rubber composition further comprises an antioxidant.

In the rubber composition of the present invention, it is preferable that the rubber composition further comprises a filler.

Further, the present invention provides a cross-linked rubber obtained by cross-linking the rubber composition as mentioned above.

EFFECTS OF INVENTION

[0013] According to the present invention, it is possible to provide an acrylic rubber capable of realizing excellent storage stability while keeping normal physical properties good, and a rubber composition containing the acrylic rubber, and the cross-linked rubber.

DESCRIPTION OF EMBODIMENTS

[0014] [Production method]

The method for producing an acrylic rubber of the present invention comprises: an emulsion polymerization step of emulsion polymerizing a monomer comprising a (meth)acrylic acid ester and at least one cross-linkable monomer selected from the group consisting of a carboxyl group-containing monomer, an epoxy group-containing monomer and a halogen group-containing monomer in the presence of a nonionic emulsifier and an anionic emulsifier with a polymerization initiator to

obtain a polymerized emulsion liquid; a coagulation step of coagulating the polymerized emulsion liquid by contacting with a metal sulfate to obtain a hydrous crumb; a washing step of performing washing on the hydrous crumb; and a drying step of drying the hydrous crumb that is washed. 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.

[0015] <Monomer>

The monomer used in the emulsion polymerization step of the present invention is characterized in that a (meth)acrylic acid ester is a main component. As the (meth)acrylic acid 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, and 2-methoxyethyl acrylate is still 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 used for the polymerization is preferably a main component of the monomer, and 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 used for the polymerization in the emulsion polymerization step of the present invention, other than the above-mentioned (meth)acrylic acid ester, a cross-linkable monomer and other copolymerizable monomers may be contained.

[0020] 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. The cross-linkable monomer is preferably a carboxyl group-containing monomer, an epoxy group-containing monomer, and a halogen atom-containing monomer, and more preferably a halogen atom-containing monomer.

[0021] 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.

[0022] 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.

[0023] 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 alkanol 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.

[0024] There is no particular limitation on the epoxy group-containing monomer. Examples of the epoxy group-containing monomer include epoxy group-containing (meth)acrylic acid ester such as glycidyl (meth)acrylate; epoxy group-containing styrene such as p-vinylbenzyl glycidyl ether; epoxy group-containing ethers such as allyl glycidyl ether, vinyl glycidyl ether, 3,4-epoxy-1-pentene, 3,4-epoxy-1-butene, 4,5-epoxy-2-pentene, 4-vinylcyclohexylglycidyl ether, cyclohexenylmethylglycidyl ether, 3,4-epoxy-1-vinylcyclohexene and allyl phenylglycidyl ether; and the like.

[0025] 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, (haloacetylcarbamoxyloxy)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.

[0026] 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 (haloacetylcarbamoxyloxy)alkyl (meth)acrylates include 2-(chloroacetylcarbamoxyloxy)ethyl (meth)acrylate, 3-(chloroacetylcarbamoxyloxy)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. Among these, an unsaturated alcohol ester of halogen-containing saturated carboxylic acid is preferable, and vinyl chloroacetate (vinyl monochloroacetate) is more preferable.

[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, mechanical properties and compression set resistance can be highly balanced when the obtained acrylic rubber is made into a cross-linked product, which is suitable.

[0028] 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 of the present invention is characterized in that a monomer containing (meth)acrylic acid ester as a main component described above is emulsion polymerized using a polymerization initiator in the presence of a nonionic emulsifier and an anionic emulsifier to obtain a polymerized emulsion liquid.

[0031] The nonionic emulsifier is not particularly limited. Examples of the nonionic emulsifier include a polyoxyalkylene alkyl

ethers such as a polyoxyethylene dodecyl ether; a polyoxyalkylene alkyl phenyl ether such as a polyoxyethylene nonylphenyl ether; a polyoxyalkylene fatty acid ester such as a polyoxyethylene stearic acid ester; a polyoxyethylene sorbitan alkyl ester; a polyoxyethylene/polyoxypropylene copolymer; and the like. Among these, a polyoxyalkylene alkyl ether, a polyoxyalkylene alkyl phenyl ether, a polyoxyethylene/polyoxypropylene copolymer are preferred, and particularly, a polyoxyethylene alkyl ether, a polyoxyethylene alkyl phenyl ether, and polyoxyethylene/polyoxypropylene copolymer are preferred. The weight-average molecular weight of the nonionic emulsifier is not particularly limited. The weight-average molecular weight of the nonionic emulsifier is usually in the range of 300 to 50,000, preferably in the range of 500 to 30,000, more preferably in the range of 1,000 to 15,000. These nonionic emulsifiers may be used alone or in combination of two or more thereof.

[0032] 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 higher alcohol sulfate ester salt such as sodium lauryl sulfate, 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 a hydrophobic group with 6 or more carbon atoms; alkyl sulfosuccinate; and the like. Among these anionic emulsifier, a phosphate ester salt and a higher alcohol sulfate ester salt are preferable, a higher alcohol phosphate ester salt and a higher alcohol sulfate ester salt are more preferable, and a higher alcohol phosphate ester salt is still more preferable. These anionic emulsifier may be used alone or in combination of two or more thereof.

[0033] The use ratio of the nonionic emulsifier and the anionic

emulsifier is usually in the range of 1/99 to 99/1, preferably in the range of 10/90 to 80/20, more preferably in the range of 25/75 to 75/25, still more preferably in the range of 50/50 to 75/25, and most preferably in the range of 65/35 to 75/25, in terms of the weight ratio of nonionic emulsifier/anionic emulsifier. By setting the ratio of the nonionic emulsifier and the anionic emulsifier to fall within this range, it is possible to reduce the amount of the metallic sulfate used as a coagulant while preventing the generation of stains due to adhesion of a polymer to a polymerization device (e.g., a polymerization tank) during emulsion polymerization. Consequently, it is possible to reduce the amount of coagulant in the finally obtained acrylic rubber. Thus, the water resistance of the obtained cross-linked rubber can be improved. Further, by setting the ratio of the nonionic emulsifier and the anionic emulsifier to fall within this range, it is possible to enhance the emulsifying action, so that it is possible to reduce the amount of emulsifier to be used. As a result, it is possible to reduce the residual amount of emulsifier contained in the acrylic rubber thus finally obtained. Accordingly, it is possible to further enhance the water resistance of the obtained acrylic rubber, which is suitable.

[0034] 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.

[0035] In the present invention, other emulsifiers may be used as needed. Other emulsifiers include, for example, a cationic emulsifier and the like. Specifically, alkyltrimethylammonium chloride, dialkylammonium chloride, benzylammonium chloride, and the like. Each of these other emulsifier may be used alone or in combination of two or more thereof. The amount of use of other emulsifier is appropriately set

within a range not impairing the object of the present invention.

[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 preferably 0.001 to 1.0 parts by weight with respect to 100 parts by weight of the monomer used in the polymerization.

[0037] When the organic peroxides and/or inorganic peroxides are used as the polymerization initiator, it is preferable to be 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 hydroxymethanesulfinic acid; 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] Each of these reducing agents may be used alone or in combination of two or more thereof. Preferably, two or more of reducing agents are used in combination. More preferably, a metal ion-containing compound in a reduced state as a first reducing agent and a reducing agent other than the metal ion-containing compound in the reduced state as a second reducing agent are combined. Still more preferably, ferrous sulfate and ascorbic acid (salt) and/or sodium formaldehyde sulfoxylate are combined. Particularly preferably, it is combined with ferrous sulfate and ascorbate. Thus, the object of the present application can be achieved more highly and is suitable. The amount of reducing agent to be used is preferably in the range of 0.0001 to 0.5 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. 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, hydroxyamine sulfate, diethylhydroxyamine, hydroxyamine 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] <Addition of compounding agent to polymerized emulsion liquid>

In the emulsion polymerization step of the present invention, various compounding agents can be added to polymerized emulsion liquid prior to coagulation, which is obtained by emulsion polymerization, if necessary, and can be uniformly dispersed in the generated acrylic rubber polymer. There is no particular limitation on the compounding agent to be added as long as it is a compounding agent for rubber. For example, antioxidant, lubricant, alkylene oxide-based polymers, and the like can be effectively blended, and are suitable.

[0046] 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.

[0047] 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 such as mono (or di or tri) (α -methylbenzyl) phenol, 2,2'-methylene-bis(6- α -methylbenzyl-*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. These antioxidants may be used alone or in combination of two or more thereof.

[0048] There is no particular limitation on the lubricant. Examples thereof include hydrocarbon-based lubricant such as liquid paraffin, paraffin wax, synthetic polyethylene wax; a fatty acid ester-based lubricant such as a stearic acid alkyl ester; fatty acid amide-based lubricant such as thearic acid amide, oleic acid amide, erucic acid amide; metallic soap-based lubricant such as calcium stearate, magnesium stearate, and zinc stearate; a phosphate ester of polyoxyethylene higher alcohol phosphates-based lubricant such as polyoxyethylene stearyl ether phosphate, polyoxyethylene lauryl ether phosphate, polyoxyethylene oleyl ether phosphate, polyoxyethylene tridecyl ether phosphate; higher fatty acid-based lubricant such as a fatty acid having 10 to 30 carbon atoms,

preferably 12 to 20 carbon atoms; and the like.

[0049] Among these, when a lubricant such as a fatty acid ester-based lubricant, a fatty acid amide-based lubricant, a phosphoric ester-based lubricant, and a higher fatty acid-based lubricant is used, preferably when a phosphoric ester-based lubricant and a higher fatty acid-based lubricant are used, more preferably when a polyoxyethylene stearyl ether phosphate is used, handling property and roll processability at the time of drying of an acrylic rubber to be produced are highly improved, which is suitable.

[0050] Each of these lubricant may be used alone or in combination of two or more thereof. The amount of lubricant to be added is appropriately set depending on the purpose of use, but is usually in the range of 0.0001 to 10 parts by weight, preferably in the range of 0.001 to 5 parts by weight, and more preferably in the range of 0.01 to 1 parts by weight, with respect to 100 parts by weight of the acrylic rubber ingredient contained in polymerized emulsion liquid.

[0051] By containing a lubricant in polymerized emulsion liquid prior to performing the coagulation, the lubricant can be well dispersed in the polymerized emulsion liquid prior to performing the coagulation. Thus, the lubricant can be contained in the acrylic rubber after coagulation in a state in which it is well dispersed. Consequently, the lubricant can be appropriately contained in the obtained acrylic rubber (suitably, lubricant can be contained in a uniformly dispersed state). Thus, it is possible to make the obtained acrylic rubber excellent in handleability and roll processability during drying. Note that, even when a lubricant is contained in a polymerized emulsion liquid prior to performing coagulation, the added lubricant is not substantially removed in the subsequent coagulation, washing, drying, and the like. Therefore, the addition effect can be sufficiently exhibited. On the other hand, when a lubricant is added after coagulation, it becomes difficult to

disperse the lubricant in the acrylic rubber. Therefore, the lubricant cannot be contained in the acrylic rubber (particularly, lubricant cannot be contained in a state in which it is uniformly dispersed). As a result, it is difficult to obtain an effect by blending a lubricant, for example, an effect of preventing adhesion and the like during drying at the time of producing an acrylic rubber.

[0052] As the alkylene oxide-based polymer, there is no particular limitation as long as it is a polymer of alkylene oxide, but a polymer of a lower alkylene oxide is usually used. Specific examples thereof include polyethylene oxide, polypropylene oxide, and ethylene oxide/propylene oxide copolymer. Among these, polyethylene oxide is suitable. The weight average molecular weight of the alkylene oxide-based polymer is selected depending on the purpose of use, but is usually in the range of 10,000 to 6,000,000, preferably in the range of 30,000 to 1,000,000, more preferably in the range of 50,000 to 500,000, particularly preferably in the range of 50,000 to 300,000, and most preferably in the range of 80,000 to 200,000. When the weight average molecular weight of the alkylene oxide-based polymer falls within this range, the object of the present invention can be highly achieved and is suitable.

[0053] These alkylene oxide-based polymers may be used alone or in combination of two or more thereof. The blending amount of the alkylene oxide-based polymer is preferably in the range of 0.01 to 1 parts by weight, more preferably in the range of 0.01 to 0.6 parts by weight, and still more preferably in the range of 0.02 to 0.5 parts by weight, with respect to 100 parts by weight of acrylic rubber ingredient in polymerized emulsion liquid. By containing an alkylene oxide-based polymer in polymerized emulsion liquid prior to coagulation, the coagulation property of a polymerized emulsion liquid can be improved. Thus, it is possible to reduce the amount of coagulant in the

coagulation step and to reduce the residual amount in the acrylic rubber finally obtained. This can enhance compression set resistance and water resistance when formed into a cross-linked rubber, and is suitable.

[0054] <Coagulation step>

A coagulation step of the present invention is characterized in that a polymerized emulsion liquid to which an antioxidant, lubricant and/or alkylene oxide-based polymer are optionally added is brought into contact with a metallic sulfate to coagulate, to obtain a hydrous crumb.

[0055] The metallic sulfate used as a coagulant is not particularly limited. For example, monovalent, divalent, and trivalent metallic sulfates can be suitably used. More preferred is monovalent or divalent metallic sulfates. Specific examples thereof include 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. Sodium sulfate, magnesium sulfate, and aluminum sulfate are preferred, and sodium sulfate and magnesium sulfate are more preferred.

[0056] Each of these metal sulfates can be used alone or as two or more types combined. The amount of the metal sulfate to be used 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 acrylic rubber ingredient in a polymerized emulsion liquid. When the metal sulfate falls within this range, storage stability and compression set resistance and water resistance when an acrylic rubber is cross-linked can be highly balanced, while sufficient coagulation of the acrylic rubber is maintained, which is suitable.

[0057] In the coagulation step of the present invention, other coagulant may be used in conjunction with metallic sulfates, if desired. Examples of other coagulants include metal chlorides 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, and tin chloride; metal nitrates 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, and tin nitrate; and the like. Each of these other coagulants may be used alone or in combination of two or more thereof. The blending amount of other coagulant is appropriately set within a range not impairing the object of the present invention.

[0058] The method of contacting a polymerized emulsion liquid with a metal sulfate may be according to a conventional method, and may be carried out by a method of adding a metal sulfate or a solution or a dispersion of a metal sulfate to a polymerized emulsion liquid, a method of charging a polymerized emulsion liquid into a solution or a dispersion of a metal sulfate, and the like. As a solution or dispersion of a metallic sulfate to which a polymerized emulsion liquid is charged, an aqueous solution is usually used. The concentration of the metallic sulfate in the aqueous solution is appropriately set depending on the purpose of 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%.

[0059] The coagulation temperature of a polymerized emulsion liquid and a metallic sulphate is not particularly limited. The contact (coagulation) temperature is usually greater than or equal to 60 °C, preferably in the range of 65 to 100 °C, more preferably in the range of 70 to 95 °C, still more preferably in the range of 78 to 95 °C, and most preferably in the range of 83 to 95 °C.

[0060] <Washing step>

The washing step of the present invention is to perform

washing on hydrous crumbs obtained in the above coagulation step.

[0061] 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.

[0062] 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.

[0063] 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.

[0064] 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.

[0065] 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. Preferably, it is added in a state of an aqueous solution having a pH of 6 or less, more preferably in a state of an aqueous solution having a pH of 5 or less, and still more preferably in a state of an aqueous solution having a pH of 4 or less. Further, the method of acid washing is not particularly limited. For example, there may be mentioned a method in which an aqueous solution of an added acid is mixed together with hydrous crumbs.

[0066] Further, the temperature at the time of acid washing is not particularly limited, but is preferably 5 to 60 °C, and more preferably 10 to 50 °C. The mixing time is 1 to 60 minutes, more preferably 2 to 30 minutes. The pH of the washing water in the acid washing is not particularly limited, and preferably a pH of 6 or less, more preferably a pH of 5 or less, and still more preferably a pH of 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.

[0067] 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.

[0068] <Drying step>

The drying step of the present invention is to perform drying on hydrous crumbs which have been washed in the above washing step.

[0069] 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.

[0070] 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.

[0071] [Acrylic rubber]

According to the present invention, an acrylic rubber of the present invention can be obtained by the above manufacturing method. Thus obtained acrylic rubber of the present invention is excellent in storage stability while keeping normal physical properties good.

[0072] The acrylic rubber of the present invention is not particularly limited except that it contains a (meth)acrylic acid ester monomer unit as a main component. When further containing a cross-linkable monomer unit, it is highly effective and suitable for the present invention.

[0073] The monomer composition in the acrylic rubber of the present invention is appropriately selected depending on the purpose of use. The content of (meth)acrylic acid ester monomer unit is usually from 50 to 99.9 wt%, preferably from 60 to 99.7 wt%, and more preferably from 70 to 99.5 wt%. The content of cross-linkable monomer unit is usually from 0.01 to 20 wt%, preferably from 0.1 to 10 wt%, and more preferably from 0.5 to 5 wt%. The content of other copolymerizable monomer unit is usually from 0 to 49.99 wt%, preferably from 0 to 39.9 wt%, and more preferably from 0 to 29.5 wt%. Examples of the (meth) acrylic ester monomer, the cross-linkable monomer, and other copolymerizable monomers

are the same as those exemplified in the above-mentioned <monomer>. Examples of cross-linkable monomer unit include a carboxyl group-containing monomer unit, a halogen group-containing monomer unit, an epoxy group-containing monomer unit, and a halogen group-containing monomer unit is preferred.

[0074] A Mooney viscosity (ML1+4, 100 °C) of acrylic rubber of the present invention is chosen according to the intended use. A Mooney viscosity (ML1+4, 100 °C) are usually in the range of 10 to 150, preferably in the range of 20 to 100, and more preferably in the range of 25 to 60.

[0075] The glass transition temperature (T_g) of acrylic rubber of the present invention is selected depending on the purpose of use, but is usually 15 °C or less, preferably 0 °C or less.

[0076] Then, according to the present invention, there is provided a method for producing such an acrylic rubber, and an acrylic rubber obtained by the production method.

In particular, the acrylic rubber of the present invention obtained by the above production method has excellent storage stability while keeping normal physical properties good. 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. According to the findings of the present inventors, the properties of the obtained acrylic rubber vary greatly depending on the state at the time of coagulation.

[0077] In the present invention, such coagulation is carried out using a metallic sulfate as a coagulant. Also, emulsion polymerization is carried out in the presence of a nonionic emulsifier and an anionic emulsifier. Therefore, at the time of coagulation, a nonionic emulsifier and an anionic emulsifier are also included. Acrylic rubbers obtained by such coagulation include a metallic sulfate, a nonionic emulsifier and

an anionic emulsifier as coagulant. However, according to the findings of the present inventor, simply including a metallic sulfate, a nonionic emulsifier and an anionic emulsifier in an acrylic rubber does not have an effect of improving storage stability while maintaining normal physical properties. The present inventor has found that it is required to use a nonionic emulsifier and an anionic emulsifier at the time of emulsion polymerization, and to be performed using a metallic sulfate as a coagulant at the time of coagulation. Then, the acrylic rubber of the present invention is obtained for the first time through such steps. The acrylic rubber of the present invention cannot be generally identified by terms such as simply including a metallic sulfate, a nonionic emulsifier and an anionic emulsifier.

[0078] Further, with respect to the acrylic rubber of the present invention, if the internal state thereof is analyzed by using various analytical instruments, each of the acrylic rubber, the nonionic emulsifier, and the anionic emulsifier includes 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.

[0079] [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, more preferably 70 wt% or more, and particularly preferably 100 wt%.

[0080] 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.

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.

[0081] 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.

[0082] 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 dithiocarbamic acid, and a carbonate thereof; a sulfur compound; a sulfur donor; a polyvalent epoxy compound; an organic carboxylic acid ammonium salt; 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 triazine compound is particularly preferred.

[0083] 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 (i.e., an acrylic rubber containing a carboxyl group-containing monomer unit as a cross-linkable monomer unit).

[0084] 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 (i.e., an acrylic rubber containing a carboxyl group-containing monomer unit as a cross-linkable monomer unit).

[0085] The organic carboxylic acid ammonium salt is, for example, ammonium benzoate and ammonium adipate. The dithiocarbamic acid compound is, for example, dimethyldithiocarbamic acid and zinc dimethyldithiocarbamate. The polyvalent carboxylic acid is, for example, tetradecanedioic acid. The isocyanuric acid compound is, for example, isocyanuric acid and ammonium isocyanurate. Among these, ammonium benzoate, dimethyldithiocarbamic acid, and isocyanuric acid are particularly suitably used in combination with an epoxy group-containing acrylic rubber (acrylic rubber containing an epoxy group-containing monomer unit as a cross-linkable monomer unit).

[0086] 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.

[0087] 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 vulcanizing 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 dithiocarbamate-based cross-linking accelerator is more preferred.

[0088] Examples of the guanidine-based vulcanizing 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.

[0089] Examples of the diazabicycloalkene-based vulcanizing accelerator include 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and the like.

[0090] Examples of the aliphatic secondary amine-based vulcanizing

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.

[0091] Examples of the aliphatic tertiary amine-based vulcanizing 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.

[0092] Examples of the dithiocarbamate-based vulcanizing accelerator include zinc dimethyldithiocarbamate, zinc diethyldithiocarbamate, zinc dibutyldithiocarbamate, zinc dipentyldithiocarbamate, zinc dihexyldithiocarbamate, zinc N-pentamethylenedithiocarbamate, zinc N-ethyl-N-phenyldithiocarbamate, zinc dibenzylthiocarbamate, 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 dibenzylthiocarbamate, and zinc N-ethyl-N-phenyldithiocarbamate are preferred.

[0093] 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 vulcanizing 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 vulcanizing accelerator such as diethyl thiourea; a thiazole vulcanizing accelerator such as 2-mercaptobenzothiazole, dibenzothiazyl disulfide, 2-mercaptobenzothiazole zinc salt; a xanthogenic acid vulcanizing accelerator such as sodium isopropyl xanthate, zinc isopropyl xanthate, zinc butyl xanthate; a thiuram vulcanizing accelerator such as tetramethylthiuram monosulfide and tetramethylthiuram disulfide; an imidazole-based vulcanizing accelerator such as 2-methylimidazole and 2-phenylimidazole; a quaternary onium salt-based vulcanizing accelerator such as tetra-n-butylammonium bromide, octadecyltri-n-butylammonium bromide; a tertiary phosphine-based vulcanizing accelerators such as triphenylphosphine and tri-p-tolylphosphine; and the like.

[0094] 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. 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.

[0095] 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.

[0096] 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.

[0097] It is suitable for the rubber composition of the present invention to further comprises 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.

[0098] 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.

[0099] 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.

[0100] The rubber composition of the present invention may further comprise 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-(triethoxysilyl)propyl)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.

[0101] 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.

[0102] The rubber composition of the present invention may include other compounding agents other than the above cross-linking agent, as well as the cross-linking accelerator, scorch retarder, filler and silane coupling agent that are used as necessary. 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.

[0103] As a method for compounding a rubber composition of the present invention, an ordinary means conventionally utilized in the polymer processing field, for example, an open roll, a Banbury mixer, various kneaders, and the like can be used.

[0104] 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.

[0105] [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.

[0106] 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.

[0107] The cross-linked rubber of the present invention is one that has excellent compression set 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 rubber 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 %.

[0108] 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.

[0109] In addition, the cross-linked rubber of the present invention is 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

[0110] 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.

[0111] [Mooney viscosity (ML1+4, 100°C)]

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

[0112] [Mooney scorch test (ML145 °C)]

The moony scorch times (t5 and t35) and Vmin of an acrylic rubber composition were measured at 145 °C according to JIS K6300. In this measurement, a time at which the Mooney viscosity increased by 5M from Vmin was set as t5, and a time at which the Mooney viscosity increased by 35M from Vmin was set as t35. Also, the acrylic rubber composition used for the measurement was made according to JIS K6299. The larger the values of t5 and t35 become, the more time it takes to vulcanize. In other words, it can be determined that the storage stability of rubber composition is excellent and the vulcanization accelerating effect is prevented (well controlled). The lower the value

of V_{min} becomes, the smaller initial vulcanization of rubber composition is. In other words, it can be determined that the storage stability is excellent.

In addition, as an accelerated test for storage stability, a Mooney scorch test (Mooney scorch test after storage) was performed on an acrylic rubber composition stored at 40 °C and 80% humidity for 3 days under the same conditions as described above. The differences between V_{min} of the Mooney scorch test after storage and V_{min} of the Mooney scorch test prior to storage were set as ΔV_{min} . The smaller the ΔV_{min} value becomes, the smaller the change in rubber composition at storage is, and it can be determined that the storage stability is excellent.

[0113] [Normal physical properties (tensile strength, elongation, hardness)]

An acrylic rubber composition was placed into a metal mold having a length of 15 cm, a width of 15 cm, and a depth of 0.2 cm. By pressing at 170 °C for 20 minutes under pressure at a press pressure of 10MPa, an acrylic rubber composition was cross-linked to obtain a sheet-shaped cross-linked rubber. The obtained cross-linked rubber was punched out with a # 3 dumbbell into a test piece. For this test piece, hardness was measured using a durometer hardness tester (Type A) according to JIS K6253. In addition, tensile strength and elongation were measured according to JIS K6251.

[0114] [Air heat aging test]

Test specimens prepared in the same manner as the test specimens used for evaluating the above normal physical properties were placed in a geer type oven for 70 hours in an environment at a temperature of 175 °C. Thereafter, the tensile strength, elongation, and hardness were measured by the same method as in the evaluation of the above normal physical properties. Evaluation of heat aging resistance

was performed by comparing the obtained results with normal physical properties measured according to the above method.

[0115] [Compression set test]

An acrylic rubber composition was molded by pressing at 170 °C for 20 minutes and cross-linked to produce a cylindrical test piece having a diameter of 29 mm and a thickness of 12.5 mm. Further, it was heated at 150 °C for 4 hours to perform secondary cross-linking. In accordance with JIS K6262, while the test piece after secondary cross-linking obtained above was compressed by 25%, it was left for 70 hours in an environment of 150 °C. Then, the compression set rate (%) was measured by releasing the compression. The smaller the value of compression set rate (%) becomes, the better compression set resistance is.

[0116] [Example 1]

To a mixing vessel equipped with a homomixer, 49.95 parts of pure water, 40.9 parts of ethyl acrylate, 35.0 parts of n-butyl acrylate, 20.0 parts of 2-methoxyethyl acrylate, 1.5 parts of acrylonitrile, 2.6 parts of vinyl monochloroacetate, 0.57 parts of sodium lauryl sulfate as an anionic emulsifier (product name "Emal 2FG", available from Kao Corporation), and 1.40 parts of a polyoxyethylene/polyoxypropylene copolymer as a nonionic emulsifier (product name "PLONON 208", available from NOF Corporation) and 0.22 parts of sodium L-ascorbate were charged. The mixture was stirred to obtain a monomer emulsion.

[0117] Then, 54.19 parts of pure water and 0.95 parts of a monomer emulsion obtained above were charged into a polymerization reaction tank equipped with a thermometer and a stirring device, and the mixture was cooled to a temperature of 15 °C under a nitrogen stream. Then, in the polymerization reaction tank, 44.74 parts of a monomer emulsion obtained above, 0.0002 parts of ferrous sulfate as a reducing agent, 0.0264 parts

of sodium ascorbate as a reducing agent, and 0.066 parts of potassium persulfate as a polymerization initiator were continuously added dropwise over a period of two 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.

[0118] To 100 parts of a polymerized emulsion liquid obtained by polymerization, 0.03 parts of mono (or di or tri) (α -methylbenzyl)phenol (product name "Nocrac SP", available from Ouchi Shinko Chemical Industrial) as an antioxidant was mixed to obtain a mixed liquid. Then, the obtained mixed liquid was transferred to a coagulation tank, and 30 parts of industrial water was added to 100 parts of the mixed liquid. After raising the temperature of the mixed liquid to 85 °C, 22 parts of magnesium sulfate was added to 100 parts of the obtained polymer (polymer contained in the polymerized emulsion liquid) while stirring the mixed liquid to coagulate the polymer. Thus, hydrous crumbs of acrylic rubber (A1) was obtained.

[0119] Then, 388 parts of industrial water was added to 100 parts of solid content of the hydrous crumbs of the obtained acrylic rubber (A1), and the mixture was stirred in a coagulation tank at room temperature for 5 minutes. Thereafter, washing of the hydrous crumbs with water was performed by discharging water content from the coagulation tank. Such an operation to wash hydrous crumbs with water was repeated 4 times in the present Example.

[0120] Then, an aqueous sulfuric acid solution (pH3) prepared 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 crumbs subjected to washing with water above, and the mixture was

stirred in a coagulation tank at room temperature for 5 minutes. Thereafter, acid washing of the hydrous crumbs was performed by discharging water content from the coagulation tank. Then, 388 parts of pure water was added to 100 parts of solid content of the hydrous crumbs subjected to acid washing, and the mixture was stirred in a coagulation tank at room temperature for 5 minutes. Then, the water was discharged from the coagulation tank to wash the hydrous crumbs with pure water. The hydrous crumbs washed with pure water was dried at 110 °C for one hour using a hot air dryer (belt conveyor type band dryer). Thus, solid acrylic rubber (A1) was obtained. At this time, adhesion of the acrylic rubber to the hot air dryer was not observed.

[0121] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A1) was 33. The composition of the acrylic rubber (A1) was 40.9 wt% of ethyl acrylate units, 35.0 wt% of n-butyl acrylate units, 20.0 wt% of methoxyethyl acrylate units, 1.5 wt% of acrylonitrile units, and 2.6 wt% of vinyl monochloroacetate units.

[0122] To 100 parts of the acrylic rubber (A1) obtained above, 60 parts of carbon black (product name "Seast 116", available from Tokai Carbon Co., Ltd.), 1 part of Stearic Acid, and 1 part of 4,4'-bis (α , α -dimethylbenzyl) diphenylamine (product name "Nocrac CD", available from Ouchi Shinko Chemical Industrial) were added, and the mixture was mixed using a Banbury mixer for 5 minutes at 50 °C. Then, to the obtained mixture, 1.0 part of zinc dibutyldithiocarbamate (product name "Nocceler BZ", available from Ouchi Shinko Chemical Industrial), 0.5 parts of 2,4,6-trimercapto-s-triazine (product name "Zisnet F", available from Sankyo Kasei Co., Ltd.) and 0.3 parts of N-cyclohexylthiophthalimide (product name "Santoguard PVI", available from Sanshin Chemical Industry Co., Ltd.) were added and kneaded. Thus, an acrylic rubber composition was obtained. According to the above method, the obtained acrylic rubber composition was subjected to a Mooney scorch test, a measurement of

hardness, tensile strength and elongation at break, an air heat aging test, and a compression set test. The results are shown in Table 1.

[0123] [Example 2]

In place of 22 parts of magnesium sulfate as a coagulant, 100 parts of sodium sulfate was used. Except for this, acrylic rubber (A2) was obtained in the same manner as in Example 1.

The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A2) was 33. The composition of the acrylic rubber (A2) was 40.9 wt% of ethyl acrylate units, 35.0 wt% of n-butyl acrylate units, 20.0 wt% of methoxyethyl acrylate units, 1.5 wt% of acrylonitrile units, and 2.6 wt% of vinyl monochloroacetate units.

Using the obtained acrylic rubber (A2), an acrylic rubber composition was obtained in the same manner as in Example 1. To the obtained acrylic rubber composition, a Mooney scorch test, a measurement of hardness, tensile strength and elongation at break, an air heat aging test, and a compression set test were performed. The results are shown in Table 1.

[0124] [Example 3]

As for the monomer composition and the polymerization step, in the same manner as in Example 1, a polymerized emulsion liquid was obtained. To 100 parts of the polymerized emulsion liquid obtained by polymerization, 0.06 parts of mono (or di, or tri) (α -methylbenzyl)phenol (product name "Laditex SP-50E", available from Higashi Chemical Co., Ltd., a 50 wt% aqueous dispersion) as antioxidant was mixed to obtain a mixed liquid. Then, 30 parts of industrial water was added to 100 parts of the obtained mixed liquid, and the temperature was adjusted to 80 °C. The polymer was coagulated by continuously adding 110 parts of a 20 wt% aqueous magnesium sulfate solution (22 parts in terms of magnesium sulfate) as coagulant. Thus, hydrous crumbs of acrylic rubber (A3) was obtained.

[0125] Then, in the same manner as in Example 1, washing with water, acid washing, washing with pure water, and drying of hydrous crumbs were performed to obtain solid acrylic rubber (A3). At this time, adhesion of the acrylic rubber to the hot air dryer was not observed.

[0126] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A3) was 33. The composition of the acrylic rubber (A3) was 40.9 wt% of ethyl acrylate units, 35.0 wt% of n-butyl acrylate units, 20.0 wt% of methoxyethyl acrylate units, 1.5 wt% of acrylonitrile units, and 2.6 wt% of vinyl monochloroacetate units.

Using the obtained acrylic rubber (A3), an acrylic rubber composition was obtained in the same manner as in Example 1. The obtained acrylic rubber composition was subjected to a Mooney scorch test, a measurement of hardness, tensile strength and elongation at break, an air heat aging test, and a compression set test. The results are shown in Table 1.

[0127] [Example 4]

In place of 22 parts of magnesium sulfate as coagulant, 500 parts of 20 wt% aqueous sodium sulfate solution (100 parts in terms of sodium sulfate) was used. Except for that, acrylic rubber (A4) was obtained in the same manner as in Example 1.

[0128] The moony viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A4) was 33. The composition of the acrylic rubber (A4) was 40.9 wt% of ethyl acrylate units, 35.0 wt% of n-butyl acrylate units, 20.0 wt% of methoxyethyl acrylate units, 1.5 wt% of acrylonitrile units, and 2.6 wt% of vinyl monochloroacetate units.

Using the obtained acrylic rubber (A4), an acrylic rubber composition was obtained in the same manner as in Example 1. The obtained acrylic rubber composition was subjected to a Mooney scorch test, a measurement of hardness, tensile strength and elongation at break, an air heat aging test, and a compression set test. The results

are shown in Table 1.

[0129] [Example 5]

In place of sodium lauryl sulfate as an anionic emulsifier, a sodium salt of a polyoxyethylene alkylphenolic phosphate ester (product name "Phosphanol LO-529", available from Toho Chemical Co., Ltd., a phosphate ester of a higher alcohol having a hydrophobic group with 15 carbon atoms) was used. Except for this, a solid acrylic rubber (A5) was obtained in the same manner as in Example 1.

[0130] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A5) was 33. The composition of the acrylic rubber (A5) was 40.9 wt% of ethyl acrylate units, 35.0 wt% of n-butyl acrylate units, 20.0 wt% of methoxyethyl acrylate units, 1.5 wt% of acrylonitrile units, and 2.6 wt% of vinyl monochloroacetate units.

Using the obtained acrylic rubber (A5), an acrylic rubber composition was obtained in the same manner as in Example 1. The obtained acrylic rubber composition was subjected to a Mooney scorch test, a measurement of hardness, tensile strength and elongation at break, an air-thermal aging test, and a compression set test. The results are shown in Table 1.

[0131] [Example 6]

In place of sodium lauryl sulfate as an anionic emulsifier, a sodium salt of polyoxyethylene alkyl ether phosphate ester (product name "Phosphanol RA-600", phosphate ester salt of a higher alcohol having a hydrophobic group (alkyl group) with 6 to 10 carbon atoms, available from Toho Chemical Co., Ltd.) was used. Except for this, a solid acrylic rubber (A6) was obtained in the same manner as in Example 1.

[0132] The Mooney viscosity (ML1+4, 100 °C) of the obtained acrylic rubber (A6) was 33. The composition of the acrylic rubber (A6) was 40.9 wt% of ethyl acrylate units, 35.0 wt% of n-butyl acrylate units, 20.0 wt% of methoxyethyl acrylate units, 1.5 wt% of acrylonitrile units, and

2.6 wt% of vinyl monochloroacetate units.

Using the obtained acrylic rubber (A6), an acrylic rubber composition was obtained in the same manner as in Example 1. The acrylic rubber composition was subjected to Mooney scorch measure, determination of hardness, tensile strength and elongation at break, air-thermal aging test, and compression set test. The results are shown in Table 1.

[0133] [Comparative Example 1]

In place of 22 parts of magnesium sulfate as coagulant, 4 parts of calcium chloride was used. Except for this, a solid acrylic rubber (C1) was obtained in the same manner as in Example 1.

[0134] The obtained acrylic rubber (C1) had a Mooney viscosity (ML1+4, 100 °C) of 33. The composition of the acrylic rubber (C1) was 40.9 wt% of ethyl acrylate units, 35.0 wt% of n-butyl acrylate units, 20.0 wt% of methoxyethyl acrylate units, 1.5 wt% of acrylonitrile units, and 2.6 wt% of vinyl monochloroacetate units.

Using the obtained acrylic rubber (C1), an acrylic rubber composition was obtained in the same manner as in Example 1. The acrylic rubber composition was subjected to Mooney scorch measure, determination of hardness, tensile strength and elongation at break, air-thermal aging test, and compression set test. The results are shown in Table 1.

[0135] [Comparative Example 2]

In place of 22 parts of magnesium sulfate as coagulant, 80 parts of sodium chloride was used. Except for this, a solid acrylic rubber (C2) was obtained in the same manner as in Example 1.

[0136] The obtained acrylic rubber (C2) had a Mooney viscosity (ML1+4, 100 °C) of 33. The composition of the acrylic rubber (C2) was 40.9 wt% of ethyl acrylate units, 35.0 wt% of n-butyl acrylate units, 20.0 wt% of methoxyethyl acrylate units, 1.5 wt% of acrylonitrile units, and 2.6 wt% of vinyl monochloroacetate units.

Using the obtained acrylic rubber (C2), an acrylic rubber

composition was obtained in the same manner as in Example 1. The acrylic rubber composition was subjected to Mooney scorch measure, determination of hardness, tensile strength and elongation at break, air-thermal aging test, and compression set test. The results are shown in Table 1.

[0137] Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2
Monomer composition	Ethyl acrylate (parts)	40.9	40.9	40.9	40.9	40.9	40.9	40.9
	n-Butyl acrylate (parts)	35	35	35	35	35	35	35
	2-Methoxyethyl acrylate (parts)	20	20	20	20	20	20	20
	Acrylonitrile (parts)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Anionic emulsifier	Vinyl monochloroacetate (parts)	2.6	2.6	2.6	2.6	2.6	2.6	2.6
		Emal 2FG	Emal 2FG	Emal 2FG	Phosphanol LO-529	Sodium salt of Phosphanol RA-600	Emal 2FG	Emal 2FG
Additive (antioxidant)		Nocrac SP	Nocrac SP	Nocrac SP	Nocrac SP	Nocrac SP	Nocrac SP	Nocrac SP
	Coagulant used in coagulation step	MgSO ₄	Na ₂ SO ₄	MgSO ₄ (#1)	Na ₂ SO ₄ (#2)	MgSO ₄	CaCl ₂	NaCl
	Amount of coagulant used with respect to 100 parts of polymer	22	100	22	100	22	4	80
		A1	A2	A3	A4	A5	A6	C1
Formulation of acrylic rubber composition	Acrylic rubber used (parts)	100						
	Stearic acid (parts)	1						
	Seast 116 (parts)	60						
	Nocrac CD (parts)	1						
	Nocceler BZ (parts)	1						
	Zisnet F (parts)	0.5						
Mooney scorch test (ML 145 °C)	Santoguard PVI (parts)	0.3						
Evaluation	t5 (min)	8.0	5.4	8.2	5.5	9.5	8.9	5.2
	t35 (min)	11.9	9.1	12.1	9.3	14.8	14	8
	Vmin	37	37	36	37	36	37	40
	Mooney scorch test after storage (40 °C, 80% humidity, 3 days later → ML145 °C)							
	t5 (min)	6.6	5.5	6.8	5.5	6.9	6.8	4.9
	t35 (min)	10.6	9.7	10.7	9.6	10.9	10.8	8.1
	Vmin	50	59	50	57	48	49	69
	ΔVmin	13	22	14	20	12	12	29
	Normal physical properties (press vulcanization 170 °C, 20 minutes)							
	Tensile strength (MPa)	9.8	10.2	9.9	10.0	10.1	10.0	9.8
	Elongation (%)	200	160	190	170	190	200	170
	Hardness	71	71	70	71	70	71	71
	Air heat aging test (press vulcanization 170 °C, 20 minutes → 175 °C, 70 hours)							
	Tensile strength (MPa)	11.6	11.6	11.5	11.6	11.6	11.5	11.8
	Elongation (%)	200	190	202	200	190	200	180
	Hardness	75	73	75	73	73	74	76
	Compression set test (%)	21	23	20	21	20	20	23

(*1) added as a 20 wt% aqueous solution

(*2) added as a 20 wt% aqueous solution

[0138] From Table 1, a cross-linkable acrylic rubber produced by polymerizing a monomer containing cross-linkable monomer using a redox catalyst in the presence of a nonionic emulsifier and an anionic emulsifier and coagulating with a metallic sulfate (Examples 1 to 6) is quite comparable in normal physical properties, the air thermal aging test, and the compression set test of the cross-linked product compared with those obtained by coagulating with a conventionally used coagulant (Comparative Examples 1 and 2).

[0139] On the other hand, in the Mooney scorch test, the acrylic rubber produced according to the present invention can prevent nearly 10 % as compared with the prior art with respect to its initial properties (V_{min} : smaller one is better). In addition, long-term properties (t_5 and t_{35} : the longer is better) are improved by nearly 10 to 50 % compared with the prior art. Therefore, it can be seen that the acrylic rubber produced in the present invention has remarkably improved storage stability. In addition, in the test of Mooney scorch after storage, it can be seen that the acrylic rubber (Examples 1 to 4) produced in the present invention exhibits the same results as described above and is also greatly improved in V_{min} change. Furthermore, among the acrylic rubbers produced in the present invention, it can be seen that, among the acrylic rubbers produced in the present invention, those using the divalent metal sulfate (Examples 1 and 3) have a higher effect than those using the monovalent metal sulfate.

CLAIMS

1. A method for producing an acrylic rubber comprising:
 - an emulsion polymerization step of emulsion polymerizing a monomer comprising a (meth)acrylic acid ester and at least one cross-linkable monomer selected from the group consisting of a carboxyl group-containing monomer, an epoxy group-containing monomer and a halogen group-containing monomer in the presence of a nonionic emulsifier and an anionic emulsifier with a polymerization initiator to obtain a polymerized emulsion liquid;
 - a coagulation step of coagulating the polymerized emulsion liquid by contacting with a metal sulfate to obtain a hydrous crumb;
 - a washing step of performing washing on the hydrous crumb;
 - and
 - a drying step of drying the hydrous crumb that is washed.
2. The method for producing the acrylic rubber according to claim 1, wherein the use ratio of the nonionic emulsifier and the anionic emulsifier is in the range of 1/99 to 99/1 in terms of a weight ratio of the nonionic emulsifier/the anionic emulsifier.
3. The method for producing the acrylic rubber according to claim 1 or 2, wherein the use ratio of the nonionic emulsifier and the anionic emulsifier is in the range of 50/50 to 75/25 in terms of a weight ratio of the nonionic emulsifier/the anionic emulsifier.
4. The method for producing the acrylic rubber according to any one of claims 1 to 3, wherein the polymerization initiator is used in combination with a reducing agent.

5. The method for producing the acrylic rubber according to claim 4, wherein at least two compounds are used as the reducing agent.

6. The method for producing the acrylic rubber according to claim 4, wherein the metal ion-containing compound in a reduced state and a reducing agent other than the metal ion-containing compound in the reduced state are used in combination as the reducing agent.

7. The method for producing the acrylic rubber according to claim 6, wherein the metal ion-containing compound in the reduced state is ferrous sulfate.

8. The method for producing the acrylic rubber according to claim 6 or 7, wherein the reducing agent other than the metal ion-containing compound in the reduced state is sodium formaldehyde sulfoxylate, ascorbic acid or ascorbate.

9. The method for producing the acrylic rubber according to claim 6 or 7, wherein the reducing agent other than the metal ion-containing compound in the reduced state is ascorbate.

10. The method for producing the acrylic rubber according to any one of claims 1 to 9, wherein the polymerization initiator is an organic peroxide or an inorganic peroxide.

11. The method for producing the acrylic rubber according to any one of claims 1 to 10, wherein contacting the polymerized emulsion liquid with the metal sulfate is carried out in a manner of adding the metal sulfate to the polymerized emulsion liquid or in a manner of adding the polymerized emulsion liquid into a solution of the metal

sulfate or a dispersion of the metal sulfate.

12. The method for producing the acrylic rubber according to any one of claims 1 to 11, wherein a contacting temperature of the polymerized emulsion liquid and the metal sulfate is 60 °C or higher.

13. The method for producing the acrylic rubber according to any one of claims 1 to 12, wherein the metal sulfate is a monovalent or divalent metal sulfate.

14. The method for producing the acrylic rubber according to any one of claims 1 to 13, wherein the anionic emulsifier is a phosphate ester salt.

15. The method for producing the acrylic rubber according to any one of claims 1 to 14, wherein the washing comprises acid washing.

16. An acrylic rubber produced by the method according to any one of claims 1 to 15.

17. The acrylic rubber of claim 16, wherein a monomer composition is 50 to 99.9 wt% of (meth)acrylic acid ester monomer units, 0.01 to 20 wt% of cross-linkable monomer units, and 0 to 49.99 wt% of other copolymerizable monomer units.

18. The acrylic rubber according to claim 16 or 17, wherein a Mooney viscosity (ML1+4, 100 °C) is in the range of 10 to 150.

19. 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 16 to 18.

20. The rubber composition according to claim 19, wherein the cross-linking agent is at least one selected from the group consisting of a polyvalent amine compound, a polyvalent epoxy compound, a polyvalent carboxylic acid, an organic carboxylic acid ammonium salt, an organic carboxylic acid metal salt, an isocyanuric acid compound, a triazine compound, and a metal soap/sulfur.

21. The rubber composition according to claim 20, further comprising a cross-linking accelerator.

22. The rubber composition according to claim 21, wherein the cross-linking accelerator is at least one selected from the group consisting of 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 vulcanizing accelerator.

23. The rubber composition according to claim 21 or 22, further comprising a scorch inhibitor.

24. The rubber composition of any one of claims 19 to 23, further comprising an antioxidant.

25. The rubber composition of any one of claims 19 to 24, further comprising a filler.

26. A cross-linked rubber obtained by cross-linking the rubber

composition according to any one of claims 19 to 25.