

{Description}

{Title of Invention}

METHOD FOR PRODUCING DIP-FORMED ARTICLE, AND DIP-FORMED
ARTICLE

5

{Technical Field}

{0001}

The present invention relates to a method for producing
a dip-formed article, and a dip-formed article. More
10 specifically, the present invention relates to a method for
producing a dip-formed article generating no crack in a
beading portion and having high tear strength, and a dip-
formed article produced by this production method.

{Background Art}

15 {0002}

Conventionally, it has been known to dip-form a dip-
forming composition containing a latex of natural rubber to
obtain a dip-formed article such as a nipple, a balloon, a
glove, a medical balloon, a sack, or the like, which is used
20 in contact with a human body. However, a latex of natural
rubber contains proteins to cause an allergic symptom to a
human body, and therefore has a problem as a dip-formed
article in direct contact with the mucous membrane or organs
of the body in some cases. Therefore, consideration for
25 using a latex of synthetic polyisoprene polymer in place of a
latex of natural rubber has been made.

{0003}

However, a dip-formed article obtained from a synthetic polyisoprene latex has poorer tear strength in a case of being used as a glove than a case where a dip-formed article
5 obtained from a latex of natural rubber is used as a glove, and therefore may be torn when the glove is attached or detached or medical practice is performed. Therefore, development of a glove with a synthetic polyisoprene latex having high tear strength has been desired.

10 {0004}

As a method for improving strength of a glove, for example, Patent Literature 1 discloses a method of using a specific vulcanization accelerator, and Patent Literature 2 discloses a method of using a salt of a styrene-maleic acid
15 monoester polymer. However, these methods improve tensile strength, but do not improve tear strength sufficiently. Therefore, a method for prolonging an aging step called pre-vulcanization, a method for increasing a vulcanization density such as strengthening full vulcanization, or the like
20 has been studied.

{0005}

However, when a vulcanization density is increased excessively, there is a problem that a crack is easily generated in a beading portion of a glove. Further, when a
25 crack is generated in a beading portion, in addition to poor appearance of a glove, the glove is easily torn from the

crack portion, resulting in lowering of tear strength.
Therefore, development of a dip-formed article having high
tear strength and generating no crack in a beading portion
has been desired.

5

{Citation List}

{Patent Literature}

{0006}

Patent Literature 1: JP 2009-209229 A

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Patent Literature 2: JP 2011-219543 A

{Summary of Invention}

{Technical Problem}

{0007}

15

An object of the present invention is to provide a
method for producing a dip-formed article generating no crack
in a beading portion and having high tear strength, and a
dip-formed article generating no crack in a beading portion
and having high tear strength.

20

{Solution to Problem}

{0008}

25

The present inventors made intensive studies in order
to solve the above problems. As a result, the present
inventors have found that the above object can be achieved by
performing the following steps (i) to (iii) in this order

with a dip-forming composition containing a synthetic polyisoprene latex, a vulcanizing agent, and a vulcanization accelerator, and have completed the present invention.

(i) Step of performing pre-vulcanization until a Swell Index

5 in toluene becomes a predetermined value or less

(ii) Step of forming a film on a surface of a mold using a mold having a surface temperature of a predetermined temperature or higher

(iii) Step of performing vulcanization at 100°C to 140°C

10 {0009}

That is, the present invention provides:

(1) a method for producing a dip-formed article

including a pre-vulcanization step of subjecting a dip-forming composition containing a synthetic polyisoprene latex,

15 a vulcanizing agent, and a vulcanization accelerator to pre-vulcanization until a Swell Index in toluene becomes 25 or less at a temperature of 30°C or higher, a film formation step of dipping a mold having a surface temperature of 60°C or higher in the dip-forming composition which has been

20 subjected to pre-vulcanization in the pre-vulcanization step to form a film on a surface of the mold, and a full vulcanization step of vulcanizing the film at a vulcanization temperature of 100°C to 140°C;

(2) the method for producing a dip-formed article

25 described in (1), in which pre-vulcanization is performed in the pre-vulcanization step until the Swell Index in toluene

becomes 17 or less;

(3) the method for producing a dip-formed article described in (1) or (2), in which the surface temperature of the mold in the film formation step is 65°C or higher;

5 (4) the method for producing a dip-formed article described in any one of (1) to (3), in which the vulcanization temperature in the full vulcanization step is 110°C to 130°C; and

(5) A dip-formed article obtained by the method for
10 producing a dip-formed article described in any one of (1) to (4).

{Advantageous Effects of Invention}

{0010}

15 The present invention provides a method for producing a dip-formed article generating no crack in a beading portion and having high tear strength, and a dip-formed article generating no crack in a beading portion and having high tear strength.

20

{Description of Embodiments}

{0011}

Hereinafter, a method for producing a dip-formed article according to the present invention will be described.

25 The method for producing a dip-formed article according to the present invention includes a pre-vulcanization step of

subjecting a dip-forming composition containing a synthetic polyisoprene latex, a vulcanizing agent, and a vulcanization accelerator to pre-vulcanization until a Swell Index in toluene becomes 25 or less at a temperature of 30°C or higher, 5 a film formation step of dipping a mold having a surface temperature of 60°C or higher in the dip-forming composition which has been subjected to pre-vulcanization in the pre-vulcanization step to form a film on a surface of the mold, and a full vulcanization step of vulcanizing the film at a 10 vulcanization temperature of 100°C to 140°C.

{0012}

(Dip-forming composition)

A dip-forming composition used in the present invention contains a synthetic polyisoprene latex, a vulcanizing agent, 15 and a vulcanization accelerator.

{0013}

(Synthetic polyisoprene latex)

A synthetic polyisoprene latex used for the dip-forming composition is a latex of a synthetic polyisoprene obtained 20 by polymerizing isoprene.

{0014}

The synthetic polyisoprene may be obtained by copolymerizing isoprene and another ethylenically unsaturated monomer copolymerizable with isoprene. A content of an 25 isoprene unit in the synthetic polyisoprene is preferably 70% by weight or more, more preferably 90% by weight or more,

still more preferably 95% by weight or more, and particularly preferably 100% by weight (homopolymer of isoprene) with respect to total monomer units because a dip-formed article having flexibility and excellent tensile strength can be easily obtained.

{0015}

Examples of the other ethylenically unsaturated monomer copolymerizable with isoprene include a conjugated diene monomer other than isoprene, such as butadiene, chloroprene, or 1,3-pentadiene; an ethylenically unsaturated nitrile monomer such as acrylonitrile, methacrylonitrile, fumaronitrile, or α -chloro acrylonitrile; a vinyl aromatic monomer such as styrene or alkyl styrene; an ethylenically unsaturated carboxylate monomer such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, or 2-ethylhexyl (meth)acrylate; and a crosslinking monomer such as divinylbenzene, diethylene glycol di(meth)acrylate, or pentaerythritol (meth)acrylate. Note that, these other ethylenically unsaturated monomers copolymerizable with isoprene may be used alone or in combination of two or more kinds thereof.

{0016}

As the isoprene unit in the synthetic polyisoprene, four types of cis-bond units, trans-bond units, 1,2-vinyl bond units, and 3,4-vinyl bond units exist depending on a bonding state of isoprene.

{0017}

A content ratio of the cis-bond units in the isoprene units contained in the synthetic polyisoprene is preferably 70% by weight or more, more preferably 90% by weight or more, and particularly preferably 95% by weight or more with respect to total isoprene units from a viewpoint of improving tensile strength of a dip-formed article.

{0018}

A weight average molecular weight of the synthetic polyisoprene is 10,000 to 5,000,000, preferably 500,000 to 5,000,000, and particularly preferably 800,000 to 3,000,000 in terms of standard polystyrene by gel permeation chromatographic analysis. When the weight average molecular weight of the synthetic polyisoprene is too small, the tensile strength of a dip-formed article tends to be lowered. On the contrary, when the weight average molecular weight of the synthetic polyisoprene is too large, production of a latex of the synthetic polyisoprene tends to be difficult.

{0019}

Further, a polymer Mooney viscosity of the synthetic polyisoprene [ML₁₊₄, 100°C] is 50 to 80, preferably 60 to 80, and particularly preferably 70 to 80.

{0020}

Further, a volume average particle diameter of a latex particle (synthetic polyisoprene particle) in the synthetic polyisoprene latex is preferably 0.5 to 10 μm, more

preferably 0.5 to 3 μm , and particularly preferably 0.5 to 2 μm . When the volume average particle diameter is too small, sometimes a latex viscosity becomes too high and handling becomes difficult. On the contrary, when the volume average particle diameter is too large, a coating may be generated on a surface of the latex during storage of the synthetic polyisoprene latex.

{0021}

An electroconductivity of the synthetic polyisoprene latex is preferably 1.0 mS/cm to 2.0 mS/cm. When the electroconductivity is less than 1.0 mS/cm, a large amount of aggregates may be generated during emulsification or concentration. When the electroconductivity is more than 2.0 mS/cm, foaming occurs severely during removal of a solvent, or foaming occurs severely during transportation or blending of the dip-forming composition, and a defect such as a pinhole may be left in a glove.

{0022}

Note that, the electroconductivity is a value measured using an electroconductivity meter (product name: SG78-FK2) manufactured by METTLER-TOLEDO at a measurement temperature of 25°C.

{0023}

A total content of an alicyclic hydrocarbon solvent and an aromatic hydrocarbon solvent for the synthetic polyisoprene latex is preferably 500 ppm by weight or less.

Further, as the alicyclic hydrocarbon solvent, cyclohexane is preferable, while as the aromatic hydrocarbon solvent, toluene is preferable. When the total content of the alicyclic hydrocarbon solvent and the aromatic hydrocarbon solvent is too large, particularly when the total content of cyclohexane and toluene is too large, the dip-forming composition tends to have a sharp odor.

{0024}

Here, the alicyclic hydrocarbon solvent and the aromatic hydrocarbon solvent are each an organic solvent for dissolving or finely dispersing the synthetic polyisoprene in producing the synthetic polyisoprene latex, described below.

{0025}

Note that, the total content of the alicyclic hydrocarbon solvent and the aromatic hydrocarbon solvent can be measured by a generally available measuring method such as a gas chromatography method.

{0026}

Examples of a method for producing a synthetic polyisoprene latex include (1) a method for producing a synthetic polyisoprene latex by emulsifying a solution or a fine suspension of a synthetic polyisoprene obtained by dissolving or finely dispersing synthetic polyisoprene in an organic solvent in the presence of a surfactant in water, and removing the organic solvent, if necessary, and (2) a method for producing a synthetic polyisoprene latex directly by

subjecting isoprene alone or a mixture of isoprene and an ethylenically unsaturated monomer copolymerizable with isoprene to emulsion polymerization or suspension polymerization. However, the production method of the above

5 (1) is preferable from a viewpoint that a synthetic polyisoprene having a high ratio of cis-bond units in isoprene units can be used and a dip-formed article having an excellent tensile strength can be obtained.

{0027}

10 A synthetic polyisoprene can be obtained by a conventionally known method, for example, by subjecting isoprene to solution polymerization in an inert polymerization solvent using a Ziegler type polymerization catalyst formed of trialkylaluminum-titanium tetrachloride or
15 an alkyl lithium polymerization catalyst such as n-butyl lithium or sec-butyl lithium. The resulting synthetic polyisoprene polymer solution may be used as it is. However, a solid synthetic polyisoprene may be taken out from the polymer solution, and then the solid synthetic polyisoprene
20 may be dissolved in an organic solvent to be used.

{0028}

At this time, after the polyisoprene is synthesized, impurities such as a residue of the polymerization catalyst remaining in the polymer solution may be removed. Further,
25 an anti-aging agent described below may be added to the solution during or after polymerization.

Further, a commercially available solid synthetic polyisoprene may also be used.

{0029}

Examples of the organic solvent used in the production method of the above (1) include an aromatic hydrocarbon solvent such as benzene, toluene, or xylene; an alicyclic hydrocarbon solvent such cyclopentane, cyclopentene, cyclohexane, or cyclohexene; an aliphatic hydrocarbon solvent such as pentane, hexane, or heptane; and a halogenated hydrocarbon solvent such as methylene chloride, chloroform, or ethylene dichloride. Among them, the aromatic hydrocarbon solvent and the alicyclic hydrocarbon solvent are preferable, and cyclohexane and toluene are particularly preferable.

Note that, a use amount of the organic solvent is preferably 2,000 parts by weight or less, and more preferably 20 to 1,500 parts by weight with respect to 100 parts by weight of the synthetic polyisoprene.

{0030}

Examples of the surfactant used in the production method of the above (1) include a nonionic surfactant such as polyoxyethylene alkyl ether, polyoxyethylene alkylphenol ether, polyoxyethylene alkyl ester, or polyoxyethylene sorbitan alkyl ester; an anionic surfactant such as a sodium or potassium salt of a fatty acid such as lauric acid, myristic acid, palmitic acid, oleic acid, linolenic acid, or rosin acid, an alkyl benzene sulfonate such as sodium dodecyl

benzene sulfonate, a higher alcohol sulfate, or an alkyl sulfosuccinate; a cationic surfactant such as alkyl trimethyl ammonium chloride, dialkyl dimethyl ammonium chloride, or alkyl benzyl dimethyl ammonium chloride; and a

5 copolymerizable surfactant such as a sulfonate of α,β -unsaturated carboxylic acid, a sulfate of α,β -unsaturated carboxylic acid, or sulfoalkyl aryl ether. However, the anionic surfactant is suitable, and sodium rosinate and sodium dodecyl benzene sulfonate are particularly preferable.
10 Note that, these surfactants may be used alone or in combination of two or more kinds thereof.

{0031}

A use amount of the surfactant is preferably 0.5 to 50 parts by weight, and more preferably 0.5 to 30 parts by
15 weight with respect to 100 parts by weight of the synthetic polyisoprene. When the amount is too small, stability of the latex tends to be poor. On the contrary, when the amount is too large, forming occurs easily, and a problem may occur during dip-forming.

20 {0032}

An amount of water used in the production method of the above (1) is preferably 50 to 5,000 parts by weight, and more preferably 100 to 3,000 parts by weight with respect to 100 parts by weight of the synthetic polyisoprene.

25 {0033}

Examples of the type of water used include hard water,

soft water, ion exchanged water, distilled water, and zeolite water. Further, a polar solvent represented by an alcohol such as methanol may be used together with water.

{0034}

5 As an apparatus used for emulsifying an organic solvent solution or a fine suspension of a synthetic polyisoprene in the presence of a surfactant in water, an apparatus commercially available generally as an emulsifier or a disperser can be used without any particular limitation. A
10 method for adding the surfactant is not particularly limited. The surfactant may be added in advance to water and/or an organic solvent solution or a fine suspension of a synthetic polyisoprene, or may be added to an emulsified liquid in the middle of an emulsification operation. The surfactant may be
15 added all together, or added in batches.

{0035}

Examples of the emulsifying apparatus include a batch type emulsifier such as product name "Homogenizer" (manufactured by IKA Co., Ltd.), product name "Polytron" (manufactured by Kinematica Co., Ltd.), or product name "TK
20 Auto Homo Mixer" (manufactured by Tokushu Kika Kogyo Co., Ltd.); a continuous emulsifier such as product name "TK Pipeline Homo Mixer" (manufactured by Tokushu Kika Kogyo Co., Ltd.), product name "Colloid Mill" (manufactured by Shinko
25 Pantec Co., Ltd.), product name "Thrasher" (manufactured by Nippon coke industry Co., Ltd.), product name "Trigonal Wet

Milling Machine" (manufactured by Mitsui Miike Machinery Co., Ltd.), product name "Cavitron" (manufactured by Euro-Tech Co., Ltd.), product name "Milder" (manufactured by Pacific Machinery & Engineering Co., Ltd.), or product name "Fine Flow Mill" (manufactured by Pacific Machinery & Engineering Co., Ltd.); a high-pressure emulsifier such as product name "Microfluidizer" (manufactured by Mizuho Industrial Co., Ltd.), product name "Nanomizer" (manufactured by Nanomizer Co., Ltd.), or product name "APV Gaulin" (manufactured by Gaulin Co., Ltd.); a membrane emulsifier such as a membrane emulsifier (manufactured by REICA Co., Ltd.); a vibration type emulsifier such as product name "Vibro Mixer" (manufactured by REICA Co., Ltd.); and an ultrasonic emulsifier such as product name "Ultrasonic Homogenizer" (manufactured by Branson Co., Ltd.). Note that, conditions for the emulsification operation using the emulsifying apparatus are not particularly limited. The conditions such as a treatment temperature, a treatment time, and the like may be appropriately selected so as to obtain a desired dispersion state.

{0036}

In the method of the above (1), it is preferable to obtain the synthetic polyisoprene latex by removing the organic solvent from the emulsified product which is obtained through the emulsification operation. A method for removing the organic solvent from the emulsified product is not

particularly limited, and distillation under reduced pressure, atmospheric distillation, steam distillation, centrifugation, or the like can be employed.

{0037}

5 Further, after the organic solvent is removed, distillation under reduced pressure, atmospheric distillation, centrifugation, membrane concentration, or other method may be used for a concentration operation, if necessary, in order to increase a solid content concentration of the synthetic
10 polyisoprene latex.

{0038}

 The solid content concentration of the synthetic polyisoprene latex is preferably 30 to 70% by weight, and more preferably 40 to 70% by weight. When the solid content
15 concentration is too low, synthetic polyisoprene particles may be separated during storage of the synthetic polyisoprene latex. On the contrary, when the solid content concentration is too high, the synthetic polyisoprene particles may be aggregated each other to generate a coarse aggregate.

20 {0039}

 Further, an additive such as a pH adjuster, a defoaming agent, a preservative, a crosslinking agent, a chelating agent, an oxygen scavenger, a dispersing agent, or an anti-aging agent usually blended in a field of a latex may be
25 blended to the synthetic polyisoprene latex.

{0040}

Examples of the pH adjuster include an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide; an alkali metal carbonate such as sodium carbonate or potassium carbonate; an alkali metal hydrogen carbonate such as sodium hydrogen carbonate; ammonia; and an organic amine compound such as trimethylamine or triethanolamine. However, an alkali metal hydroxide or ammonia is preferable.

{0041}

(Vulcanizing agent)

Examples of the vulcanizing agent include sulfur such as powdered sulfur, flowers of sulfur, precipitated sulfur, colloidal sulfur, surface-treated sulfur, or insoluble sulfur; and a sulfur-containing compound such as sulfur chloride, sulfur dichloride, morpholine-disulfide, alkylphenol-disulfide, N,N'-dithio-bis(hexahydro-2H-azepinone-2), phosphorus-containing polysulfide, polymer polysulfide, or 2-(4'-morpholinodithio) benzothiazole. Among them, sulfur can be preferably used. These vulcanizing agents may be used alone or in combination of two or more kinds thereof.

{0042}

A use amount of the vulcanizing agent is not particularly limited, but is preferably 0.1 to 10 parts by weight, and more preferably 0.2 to 3 parts by weight with respect to 100 parts by weight of the synthetic polyisoprene. When the amount is too small or too large, the tensile

strength of a dip-formed article tends to be lowered.

{0043}

(Vulcanization accelerator)

As the vulcanization accelerator, a vulcanization
5 accelerator usually used in dip-forming can be used.
Examples thereof include dithiocarbamic acids such as diethyl
dithiocarbamic acid, dibutyl dithiocarbamic acid, di-2-
ethylhexyl dithiocarbamic acid, dicyclohexyl dithiocarbamic
acid, diphenyl dithiocarbamic acid, or dibenzyl
10 dithiocarbamic acid, and a zinc salt thereof; 2-
mercaptobenzothiazole, zinc 2-mercaptobenzothiazole, 2-
mercapto thiazoline, dibenzothiazyl-disulfide, 2-(2,4-
dinitrophenylthio) benzothiazole, 2-(N,N-diethylthio-
carbylthio) benzothiazole, 2-(2,6-dimethyl-4-morpholinothio)
15 benzothiazole, 2-(4'-morpholino-dithio) benzothiazole, 4-
morphonilyl-2-benzothiazyl-disulfide, and 1,3-bis(2-
benzothiazyl-mercaptomethyl) urea. However, zinc diethyl
dithiocarbamate, 2-mercaptobenzothiazole, and zinc 2-
mercaptobenzothiazole are preferable. These vulcanization
20 accelerators may be used alone or in combination of two or
more kinds thereof.

{0044}

A use amount of the vulcanization accelerator is
preferably 0.05 to 5 parts by weight, and more preferably 0.1
25 to 2 parts by weight with respect to 100 parts by weight of
the synthetic polyisoprene. When the amount is small, the

tensile strength of a dip-formed article may be lowered.

When the amount is too large, the elongation and the tensile strength of a dip-formed article may be lowered.

{0045}

5 (Other components)

(Zinc oxide)

The dip-forming composition used for the present invention preferably further contains zinc oxide. A content of zinc oxide is not particularly limited, but is preferably
10 0.1 to 5 parts by weight, and more preferably 0.2 to 2 parts by weight with respect to 100 parts by weight of the synthetic polyisoprene. When the amount is too small, the tensile strength of a dip-formed article tends to be lowered. On the contrary, when the amount is too large, the stability
15 of synthetic polyisoprene particles in the dip-forming composition may be lowered to generate a coarse aggregate.

{0046}

(Dispersing agent)

The dip-forming composition used for the present
20 invention may contain a dispersing agent, if necessary. Examples of the dispersing agent include an anionic surfactant such as a sodium or potassium salt of a fatty acid such as lauric acid, myristic acid, palmitic acid, oleic acid, linolenic acid, or rosin acid, an alkyl benzene sulfonate
25 such as sodium dodecyl benzene sulfonate, a higher alcohol sulfate, or an alkyl sulfosuccinate. However, sodium dodecyl

benzene sulfonate is particularly preferable. Note that, these surfactants may be used alone or in combination of two or more kinds thereof.

{0047}

5 A use amount of the dispersing agent is preferably 0.01 to 5 parts by weight, and more preferably 0.05 to 3 parts by weight with respect to 100 parts by weight of the synthetic polyisoprene. When the amount is small, blending stability of the dip-forming composition may be lowered, or many
10 aggregates may be generated during pre-vulcanization. Further, when the amount is too large, the dip-forming composition may foam easily, and a pinhole may be generated easily.

{0048}

15 (Compounding agent)

 The dip-forming composition of the present invention can further contain a compounding agent such as an anti-aging agent; a reinforcing agent such as carbon black, silica, or talc; a filler such as calcium carbonate or clay; an
20 ultraviolet absorber; or a plasticizer, if necessary.

{0049}

 Examples of the anti-aging agent include a phenol-based anti-aging agent containing no sulfur atom, such as 2,6-di-4-methylphenol, 2,6-di-t-butylphenol, butylhydroxyanisole, 2,6-
25 di-t-butyl- α -dimethylamino-p-cresol, octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, styrenated phenol, 2,2'-

methylene-bis(6- α -methyl-benzyl-p-cresol), 4,4'-methylene bis(2,6-di-t-butylphenol), 2,2'-methylene-bis(4-methyl-6-t-butylphenol), alkylated bisphenol, or a product of a butylation reaction between p-cresol and dicyclopentadiene; a
5 thio bisphenol-based anti-aging agent such as 2,2'-thiobis-(4-methyl-6-t-butylphenol), 4,4'-thiobis-(6-t-butyl-o-cresol), or 2,6-di-t-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol; a phosphite-based anti-aging agent such as tris(nonylphenyl) phosphite, diphenyl isodecyl phosphite, or
10 tetraphenyl dipropylene glycol-diphosphite; a sulfur ester-based anti-aging agent such as dilauryl thiodipropionate; an amine-based anti-aging agent such as phenyl- α -naphthylamine, phenyl- β -naphthylamine, p-(p-toluenesulfonyl amido)-diphenylamine, 4,4'-(α,α -dimethylbenzyl) diphenylamine, N,N-
15 diphenyl-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, or a butyraldehyde-aniline condensate; a quinoline-based anti-aging agent such as 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline; and a hydroquinone-based anti-aging agent such as 2,5-di-(t-amyl) hydroquinone. These
20 anti-aging agents may be used alone or in combination of two or more kinds thereof.

{0050}

A use amount of the anti-aging agent is preferably 0.05 to 10 parts by weight, and more preferably 0.1 to 5 parts by
25 weight with respect to 100 parts by weight of the synthetic polyisoprene. When the amount is too small, a synthetic

polyisoprene may be deteriorated. Further, when the amount is too large, the tensile strength of a dip-formed article may be lowered.

{0051}

5 A method for preparing a dip-forming composition is not particularly limited. Examples of the preparation method include a method for mixing a vulcanizing agent, a vulcanization accelerator, zinc oxide, the above dispersing agent, a monovalent salt of dialkyl dithiocarbamic acids, and
10 another compounding agent blended if necessary, such as an anti-aging agent, to a latex of a synthetic polyisoprene using a disperser such as a ball mill, a kneader, or a disper; and a method for preparing an aqueous dispersion containing desired blending components other than a latex of
15 a synthetic polyisoprene in advance using the above disperser and then mixing the aqueous dispersion to a latex of a synthetic polyisoprene. Further, after the above dispersing agent and a monovalent salt of dialkyl dithiocarbamic acid are mixed to a latex of a synthetic polyisoprene in advance,
20 a vulcanizing agent, a vulcanization accelerator, and another compounding agent such as an anti-aging agent can be added.

A pH of the dip-forming composition is preferably 7 or more, and more preferably in a range of 8 to 12.

Further, a solid content concentration of the dip-
25 forming composition is preferably within a range of 15 to 65% by weight.

{0052}

(Pre-vulcanization step)

The method for producing a dip-formed article according to the present invention includes a pre-vulcanization step for aging (also referred to as pre-vulcanization) a dip-forming composition before the dip-forming composition is subjected to dip-forming. In the pre-vulcanization step of the present invention, a dip-forming composition containing a synthetic polyisoprene polymer, a vulcanizing agent, and a vulcanization accelerator is subjected to pre-vulcanization until a Swell Index in toluene becomes 25 or less, preferably 17 or less at a temperature of 30°C or higher. When the Swell Index of after pre-vulcanization is too large, the tear strength of the resulting dip-formed article is lowered.

15 {0053}

Time for pre-vulcanization is not particularly limited, but is preferably one to 14 days, and more preferably one to seven days although the time depends on a pre-vulcanization temperature. When the time is too short or too long, the tensile strength of the resulting dip-formed article tends to be lowered.

{0054}

The resulting product is preferably stored at a temperature of 10°C to 30°C after being subjected to pre-vulcanization and before being subjected to dip-forming.

When the product is stored at a high temperature, the tensile

strength of the resulting dip-formed article tends to be lowered.

{0055}

(Film formation step)

5 The method for producing a dip-formed article according to the present invention includes a film formation step for dip-forming a dip-forming composition which has been subjected to pre-vulcanization in the pre-vulcanization step. In the film formation step, by dipping a mold having a
10 surface temperature of 60°C or higher, preferably of 65°C or higher, a film is formed on a surface of the mold.

{0056}

 Here, dip-forming is a method for dipping a mold in a dip-forming composition, depositing the composition on a
15 surface of the mold, then pulling up the mold from the composition, and then drying the composition deposited on the surface of the mold.

{0057}

 In the present invention, the mold before being dipped
20 in the dip-forming composition is preheated so as to have a surface temperature of 60°C or higher, preferably 65°C or higher. When the surface temperature is too low, a crack may be generated in a beading portion in case of the resulting dip-formed article being formed into a glove.

25 {0058}

 Further, before the mold is dipped in the dip-forming

composition or after the mold is pulled up from the dip-forming composition, a coagulating agent can be used, if necessary.

{0059}

5 Specific examples of a method for using a coagulating agent include a method for dipping a mold before dipping in a dip-forming composition in a solution of a coagulating agent to deposit the coagulating agent on the mold (anode coagulant dipping method), and a method for dipping a mold on which a
10 dip-forming composition is deposited in a coagulating agent solution (teague coagulant dipping method). However, the anode coagulant dipping method is preferable from a viewpoint of obtaining a dip-formed article having less thickness unevenness.

15 {0060}

 Specific examples of the coagulating agent include a water-soluble polyvalent metal salt such as a metal halide including barium chloride, calcium chloride, magnesium chloride, zinc chloride, and aluminum chloride; a nitrate
20 including barium nitrate, calcium nitrate, and zinc nitrate; an acetate including barium acetate, calcium acetate, and zinc acetate; or a sulfate including calcium sulfate, magnesium sulfate, and aluminum sulfate. Among them, a calcium salt is preferable, and calcium nitrate is more
25 preferable.

 These water-soluble polyvalent metal salts may be used

alone or in combination of two or more kinds thereof.

{0061}

The coagulating agent is preferably used in a state of an aqueous solution. This aqueous solution may further

5 contain a water-soluble organic solvent such as methyl alcohol or ethyl alcohol, or a nonionic surfactant. A concentration of the coagulating agent is preferably 5 to 50% by weight, and more preferably 10 to 30% by weight although the concentration depends on the kind of a water-soluble
10 polyvalent metal salt.

{0062}

After the mold is pulled up from the dip-forming composition, the mold is usually heated to dry a deposit (film) formed on the mold. Drying conditions may be selected
15 appropriately.

{0063}

(Full vulcanization step)

The method for producing a dip-formed article according to the present invention includes a full vulcanization step
20 of vulcanizing the deposit (film) formed on the mold by heating the deposit (film). In the full vulcanization step, the film is vulcanized at a vulcanization temperature of 100°C to 140°C, preferably of 110°C to 130°C. When the vulcanization temperature is too high, the tear strength of
25 the resulting dip-formed article is lowered.

{0064}

Further, heating time in the full vulcanization step is preferably 10 to 120 minutes. A method for heating is not particularly limited, but examples thereof include a method for heating in a dryer, a method for heating by hot air in an oven, and a method for heating by irradiation with an infrared ray.

{0065}

Further, before heating or after heating the mold on which a dip-forming composition is deposited, the mold is preferably washed with water or warm water in order to remove water-soluble impurities (for example, excessive surfactant or coagulating agent).

{0066}

A dip-formed article after the full vulcanization step is detached from the mold. Specific examples of the detachment method include a method for peeling the dip-formed article from the mold by hand and a method for peeling the dip-formed article by hydraulic pressure or compressed air pressure. When the dip-formed article in the middle of the full vulcanization step has sufficient strength against detachment, the dip-formed article may be detached in the middle of the full vulcanization step, and continuously, the subsequent full vulcanization step may be continued.

{0067}

When the dip-formed article is a glove, in order to prevent dip-formed articles from sticking to each other at

contacting surfaces, and to improve the slip at the time of attachment or detachment, inorganic fine particles such as talc or calcium carbonate, or organic fine particles such as starch particles may be sprayed on a surface of the glove, an elastomer layer containing fine particles may be formed on the surface of the glove, or a surface layer of the glove may be chlorinated.

{Examples}

{0068}

Hereinafter, the present invention will be described in detail with Examples, but the present invention is not limited to these Examples. Note that, in the following description, "%" and "parts" are based on a weight, unless otherwise indicated. Note that, various physical properties were measured as follows.

{0069}

(Swell Index)

In Examples and Comparative Examples, a dip-forming composition which had been subjected to the pre-vulcanization step (aging) was cast into an aluminum plate with a dropper so as to obtain the composition at about 1 g in the dry state, and was dried in a vacuum dryer at room temperature under reduced pressure for three hours. The resulting dried product was cut to obtain a sample.

{0070}

This sample was weighed precisely, and was put in a 80-

mesh wire net (this weight is referred to as A). 100 mL of toluene was injected thereinto, and the resulting mixture was allowed to stand for 24 hours. After 24 hours, the 80-mesh wire net was taken out, and excessive toluene was removed.

5 Thereafter, immediately, the swollen sample was weighed precisely together with the wire net (this weight is referred to as B).

{0071}

Then, toluene was volatilized in a draft. Thereafter,
10 the sample was dried in a dryer having an internal temperature of 105°C for two hours, and a weight thereof including the wire net was measured (this weight is referred to as C). A Swell Index was determined by the following formula.

15
$$\text{Swell Index} = (B - A) / (C - A)$$

{0072}

(Crack generation status in beading portion)

In each step of Examples and Comparative Examples, the crack generation status in a beading portion was determined
20 visually.

{0073}

(Tensile strength and elongation immediately before breaking of dip-formed article)

The tensile strength of a dip-formed article was
25 measured based on ASTM D412. Specifically, a film of a dip-formed article was punched with a dumbbell (SDMK-100C:

manufactured by Dumbbell Co., Ltd.) to make a test piece for measuring tensile strength. The test piece was pulled using a Tensilon Universal Testing Machine (product name: "RTG-1210", manufactured by A & D Company, Limited) at a tensile speed of 500 mm/min, and the tensile strength immediately before breaking (unit: MPa) and elongation immediately before breaking (unit: %) were measured.

{0074}

(Tear strength of dip-formed article)

The tear strength of a dip-formed article was measured based on ASTM D624-00. Specifically, a film-shaped dip-formed article having a film thickness of about 0.2 mm was subjected to humidity adjustment in a constant temperature and constant humidity room at 23°C at a relative humidity of 50% for 24 hours or more. Thereafter, the dip-formed article was punched with a dumbbell (SDMK-1000C: manufactured by Dumbbell Co., Ltd.) to make a test piece. The test piece was pulled using a Tensilon Universal Testing Machine (product name: "RTC-1225A", manufactured by Orientec Co., Ltd.) at a tensile speed of 500 mm/min to measure tear strength (unit: N/mm).

{0075}

{Example 1}

(Dip-forming composition)

While a synthetic polyisoprene latex was stirred, sodium dodecylbenzene sulfonate having a concentration of 10%

by weight was added to the synthetic polyisoprene latex
(product name: "NIPOL ME1150" manufactured by Zeon
Corporation, homopolymer of isoprene, solid content
concentration: 61%, average particle diameter: 1.2 μm , weight
5 average molecular weight: 1,300,000, amount of cis-bond
units: 98%) such that the content of sodium dodecylbenzene
sulfonate was 1 part in terms of a solid content with respect
to 100 parts of synthetic polyisoprene polymer. Then, while
the resulting mixture was stirred, water dispersions of
10 compounding agents were added to the resulting mixture such
that the contents of zinc oxide, sulfur, an anti-aging agent
(product name: Wingstay L, manufactured by Goodyear Tire and
Rubber Company), zinc diethyl dithiocarbamate, zinc dibutyl
dithiocarbamate, and zinc 2-mercaptobenzothiazole were 1.5
15 parts, 1.5 parts, 2 parts, 0.3 parts, 0.5 parts, and 0.7
parts, respectively, in terms of a solid content with respect
to 100 parts of synthetic polyisoprene polymer in the mixture.
Thereafter, a potassium hydroxide aqueous solution was added
thereto to obtain a dip-forming composition having a pH
20 adjusted to 10.5.
{0076}

Note that, the weight average molecular weight of a
synthetic polyisoprene latex is a value calculated as an
weight average molecular weight in terms of standard
25 polystyrene by dissolving the synthetic polyisoprene latex in
tetrahydrofuran such that the solid content concentration of

the synthetic polyisoprene latex is 0.1% by weight and
subjecting this solution to gel permeation chromatographic
analysis. Further, the amount of cis-bond units is a ratio
of a cis-bond unit with respect to all isoprene units in a
5 synthetic polyisoprene, determined by drying a coagulated
product obtained by adding methanol to a synthetic
polyisoprene latex and coagulating the resulting mixture and
then subjecting the coagulated product to ^1H -NMR analysis.
{0077}

10 (Pre-vulcanization step)

The resulting dip-forming composition was subjected to
pre-vulcanization (aging) in a constant temperature water
tank adjusted to 30°C until a Swell Index became 13.
{0078}

15 (Film formation step)

A commercially available ceramic hand mold
(manufactured by Shinko Ind. Ltd.) was washed, was pre-heated
in an oven at 70°C, was then dipped in a coagulating agent
aqueous solution containing 18% by weight of calcium nitrate
20 and 0.05% by weight of polyoxyethylene lauryl ether (product
name: Emulgen 109P, manufactured by Kao Corporation) for five
seconds, and was taken out therefrom. Subsequently, the hand
mold coated with a coagulating agent was dried in an oven at
70°C for 30 minutes or more.

25 {0079}

Thereafter, the hand mold coated with a coagulating

agent was taken out from the oven, and was dipped in a dip-forming composition for 10 seconds with setting a surface temperature of the hand mold immediately before dipping to 65°C. Thereafter, the hand mold was subjected to air drying
5 at room temperature for 10 minutes, was then subjected to beading, and was further allowed to stand for 10 minutes. After 10 minutes, the crack generation status in a beading portion was determined visually, and no crack was observed.

This hand mold was dipped in warm water at 50°C for two
10 minutes. Thereafter, similarly, presence of a crack in the beading portion was determined visually, and no crack was observed.

{0080}

(Full vulcanization step)

15 Thereafter, the hand mold coated with a film-shaped synthetic polyisoprene polymer was put in an oven, and was subjected to full vulcanization at 120°C for 30 minutes. After the full vulcanization step, no crack was observed in the beading portion.

20 {0081}

 The hand mold coated with the film which had been subjected to full vulcanization was cooled to room temperature, talc was spread thereon, and then the film was peeled off from the hand mold. Measurement results of
25 tensile strength, elongation immediately before breaking, and tear strength of a resulting dip-formed article are shown in

Table 1.

{0082}

{Example 2}

A dip-formed article was produced in a similar manner to Example 1 except that aging was performed until a Swell Index became 22 in the pre-vulcanization step, and evaluation was performed similarly. The results are shown in Table 1. Note that, no crack was observed in a beading portion after beading, after dipping in warm water, or after vulcanization.

{0083}

{Example 3}

A dip-formed article was produced in a similar manner to Example 1 except that the temperature of the full vulcanization was 140°C in the full vulcanization step, and evaluation was performed similarly. The results are shown in Table 1. Note that, no crack was observed in a beading portion after beading, after dipping in warm water, or after vulcanization.

{0084}

{Comparative Example 1}

A dip-formed article was produced in a similar manner to Example 1 except that aging was terminated when a Swell Index became 27 in the pre-vulcanization step, and evaluation was performed similarly. The results are shown in Table 1. Note that, no crack was observed in a beading portion after beading, after dipping in warm water, or after vulcanization.

{0085}

{Comparative Example 2}

A dip-formed article was produced in a similar manner to Example 1 except that a hand mold was dipped in a dip-forming composition with setting a surface temperature of the hand mold to 50°C in the film formation step, and evaluation was performed similarly. The results are shown in Table 1. Note that, many cracks were observed in a beading portion after beading. Also, cracks were further increased in the beading portion during dipping in warm water and after vulcanization, and a dip-formed article having a poor appearance was obtained.

{0086}

{Comparative Example 3}

A dip-formed article was produced in a similar manner to Example 1 except that a hand mold was dipped in a dip-forming composition with setting a surface temperature of the hand mold to 55°C in the film formation step, and evaluation was performed similarly. The results are shown in Table 1. Note that, two cracks were observed in a beading portion after beading. Further, cracks were not increased in the beading portion during dipping in warm water or after vulcanization, but a dip-formed article having a poor appearance was obtained.

{0087}

{Comparative Example 4}

A dip-formed article was produced in a similar manner to Example 1 except that the temperature of the full vulcanization was 160°C in the full vulcanization step, and evaluation was performed similarly. The results are shown in Table 1. Note that, no crack was observed in a beading portion after beading, after dipping in warm water, or after vulcanization.

{0088}

{Table 1}

			Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Production conditions	Swell Index	(times)	13	22	13	27	13	13	13
	Surface temperature of hand mold	(°C)	65	65	65	65	50	55	65
	Vulcanization temperature	(°C)	120	120	140	120	120	120	160
Dip-formed article	Crack generation status in beading portion	-	Not observed	Not observed	Not observed	Not observed	Many cracks were observed	Two cracks were observed	Not observed
	Tensile strength	(MPa)	23	21	24	22	23	22	13
	Elongation immediately before breaking	(%)	900	910	910	900	900	900	880
	Tear strength	(N/mm)	35	22	28	15	30	32	11

{0089}

In the production methods of Examples 1 to 3, no crack was observed in a beading portion, and a dip-formed article having high tear strength was obtained.

{0090}

On the other hand, in Comparative Example 1 in which aging was terminated when a Swell Index became 27, no crack

was observed in a beading portion, but a dip-formed article having low tear strength was obtained.

{0091}

Further, a difference in the degree of a crack in a
5 beading portion was observed between Comparative Examples 2 and 3 in which the surface temperature of a hand mold was low. There was a tendency that the lower the surface temperature of the hand mold was, the larger the number of cracks was.

In addition, in Comparative Example 4 in which the
10 vulcanization temperature was high, no crack was observed in a beading portion, but a dip-formed article having low tensile strength and low tear strength was obtained.

{Industrial Applicability}

15 {0092}

A dip-formed article obtained by a method for producing a dip-formed article according to the present invention has no crack in a beading portion and has high tear strength. Therefore, the dip-formed article is suitable for a glove for
20 surgery, medical examination, home use, agriculture, fishery, or industry; a finger sack, or the like.

{Claims}

{Claim 1}

A method for producing a dip-formed article,
comprising:

- 5 a pre-vulcanization step of subjecting a dip-forming composition containing a synthetic polyisoprene latex, a vulcanizing agent, and a vulcanization accelerator to pre-vulcanization until a Swell Index in toluene becomes 25 or less at a temperature of 30°C or higher;
- 10 a film formation step of dipping a mold having a surface temperature of 60°C or higher in the dip-forming composition which has been subjected to pre-vulcanization in the pre-vulcanization step to form a film on a surface of the mold; and
- 15 a full vulcanization step of vulcanizing the film at a vulcanization temperature of 100°C to 140°C.

{Claim 2}

- 20 The method for producing a dip-formed article according to claim 1, wherein pre-vulcanization is performed in the pre-vulcanization step until the Swell Index in toluene becomes 17 or less.

{Claim 3}

- 25 The method for producing a dip-formed article according to claim 1 or 2, wherein the surface temperature of the mold

in the film formation step is 65°C or higher.

{Claim 4}

The method for producing a dip-formed article according
5 to any one of claims 1 to 3, wherein the vulcanization
temperature in the full vulcanization step is 110°C to 130°C.

{Claim 5}

A dip-formed article obtained by the method for
10 producing a dip-formed article according to any one of claims
1 to 4.