Claims

[Claim 1]

A modified conjugated diene-based polymer, comprising a nitrogen atom,

wherein a content of the nitrogen atom is 25 ppm by mass or more based on a total amount of the modified conjugated diene-based polymer,

a Mooney stress-relaxation rate measured at 110°C is 0.45 or less,

a modification percentage is 75% by mass or more, and

the ratio of the first weight-average molecular weight to the first number-average molecular weight is 1.50 or more and 3.50 or less, wherein the first weight-average molecular weight is the weight-average molecular weight in terms of polystyrene determined by measurement with gel permeation chromatography and the first number-average molecular weight is the number-average molecular weight in terms of polystyrene determined by measurement with gel permeation chromatography.

[Claim 2]

The modified conjugated diene-based polymer according to claim 1, comprising a nitrogen atom at one or more terminal, and

a star-shaped polymer structure having a nitrogen atom-containing alkoxysilane substituent positioned at a center thereof.

[Claim 3]

The modified conjugated diene-based polymer according to claim 1 or 2, wherein a shrinkage factor (g') determined by gel permeation chromatography (GPC)-light scattering measurement with a viscosity detector is 0.86 or less.

[Claim 4]

The modified conjugated diene-based polymer according to any one of claims 1 to 3, wherein a ratio of a second number-average molecular weight determined by GPC-light scattering measurement to a first number-average molecular weight determined by measurement with GPC is 1.00 or more.

[Claim 5]

The modified conjugated diene-based polymer according to any one of claims 1 to 4, wherein a ratio of a second weight-average molecular weight determined by GPC-light scattering measurement to a first weight-average molecular weight determined by measurement with GPC is 1.00 or more.

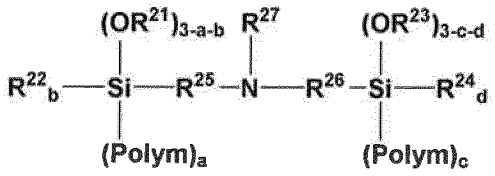
[Claim 6]

The modified conjugated diene-based polymer according to any one of claims 1 to 5, wherein

the first number-average molecular weight is 200000 or more and 2000000 or less.

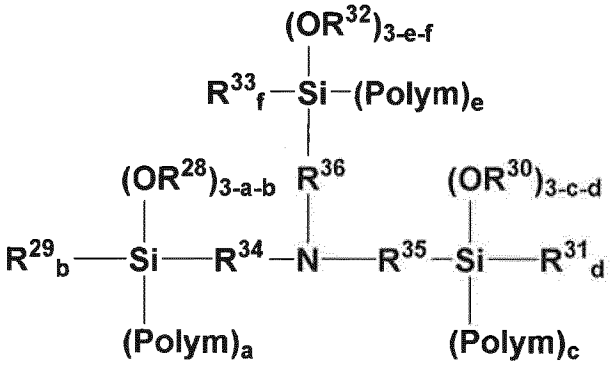
[Claim 7]

The modified conjugated diene-based polymer according to any one of claims 1 to 6, represented by following general formula (A) or (B):



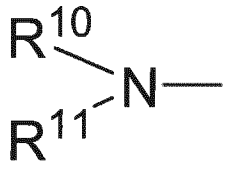
(A)

wherein R^{21} to R^{24} each independently denote an alkyl group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; R^{25} and R^{26} each independently denote an alkylene group having 1 to 20 carbon atoms; R^{27} denotes a hydrogen atom, a silyl group substituted with a hydrocarbon, an alkyl group having 1 to 20 carbon atoms, or an aryl group having 6 to 20 carbon atoms; a and c each independently denote an integer of 1 or 2; b and d each independently denote an integer of 0 or 1; (a+b) and (c+d) each independently denote an integer of 2 or less; (Polym) denotes a conjugated diene-based polymer derived by polymerization of a conjugated diene compound or copolymerization of a conjugated diene compound and an aromatic vinyl compound, wherein at least one terminal thereof is a functional group represented by any of general formulas (4) to (7) below; in a case that a plurality of moieties is present as R^{21}, R^{23}, or (Polym) they are independent of each other;



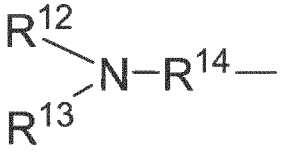
(B)

wherein R^{28} to R^{33} each independently denote an alkyl group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; R^{34} to R^{36} each independently denote an alkylene group having 1 to 20 carbon atoms; a, c, and e each independently denote an integer of 1 or 2; b, d, and f each independently denote an integer of 0 or 1; (a+b), (c+d), and (e+f) each independently denote an integer of 2 or less; (Polym) denotes a conjugated diene-based polymer derived by polymerization of a conjugated diene compound or copolymerization of a conjugated diene compound and an aromatic vinyl compound, wherein at least one terminal thereof is a functional group represented by any of following general formulas (4) to (7); in a case that a plurality of moieties is present as R^{28}, R^{30}, ,R^{32}, or (Polym) they are independent of each other;



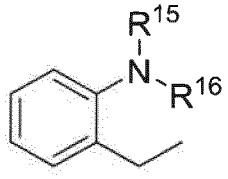
(4)

wherein R^{10} and R^{11} each independently denote at least one selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group having 3 to 14 carbon atoms, and an aralkyl group having 6 to 20 carbon atoms; R^{10} and R^{11} may be attached together to form a cyclic structure together with an adjacent an adjacentnitrogen atom, and in this case, R^{10} and R^{11} denote an alkyl group having 5 to 12 carbon atoms, and may have an unsaturated bond or a branched structure in a part thereof;



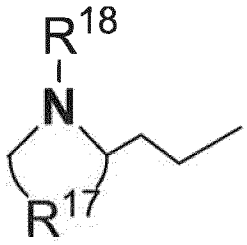
(5)

wherein R^{12} and R^{13} each independently denote at least one selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group having 3 to 14 carbon atoms, and an aralkyl group having 6 to 20 carbon; R^{12} and R^{13} may be attached together to form a cyclic structure together with an adjacentan adjacent nitrogen atom, and in this case, R^{12} and R^{13} denote an alkyl group having 5 to 12 carbon atoms, and may have an unsaturated bond or a branched structure in a part thereof; R^{14} denotes an alkylene group having 1 to 20 carbon atoms or a conjugated diene-based polymer having 1 to 20 carbon atoms;



(6)

wherein R^{15} and R^{16} each independently denote at least one selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group having 3 to 14 carbon atoms, and an aryl group having 6 to 20 carbon atoms; and R^{15} and R^{16} may be attached together to form a cyclic structure together with an adjacentan adjacent nitrogen atom, and in this case, R^{15} and R^{16} denote an alkyl group having 5 to 12 carbon atoms, and may have a branched structure in a part thereof;



(7)

wherein R^{17} denotes a hydrocarbon group having 2 to 10 carbon atoms, and may have an unsaturated bond or a branched structure in a part thereof; and R^{18} denotes an alkyl group having 1 to 12 carbon atoms, and may have a branched structure in a part thereof.

[Claim 8]

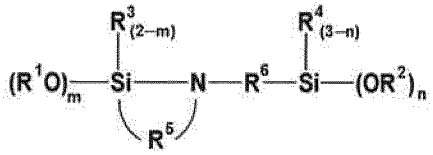
A method for producing the modified conjugated diene-based polymer according to any one of claims 1 to 7, comprising steps of:

polymerizing at least a conjugated diene compound in a presence of an organolithium compound having at least one nitrogen atom in a molecule to obtain a conjugated diene-based polymer; and

modifying the conjugated diene-based polymer with a modifier having four or more alkoxy groups bonding to a silyl group and a tertiary amino group in one molecule.

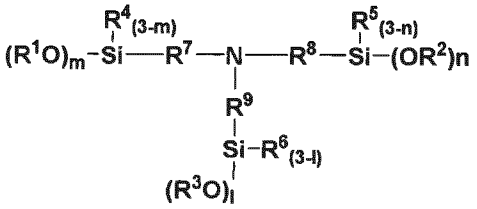
[Claim 9]

The method for producing the modified conjugated diene-based polymer according to claim 8, wherein the modifier comprises a modifier represented by any of following general formulas (1) to (3):



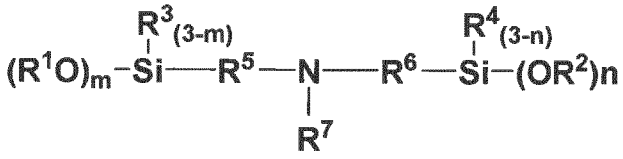
(1)

wherein R^1 to R^4 each independently denote an alkyl group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; R^5 denotes an alkylene group having 1 to 10 carbon atoms; R^6 denotes an alkylene group having 1 to 20 carbon atoms; m denotes an integer of 1 or 2; n denotes an integer of 2 or 3; (m+n) denotes an integer of 4 or more; and in a case that a plurality of moieties is present as any of R^1 to R^4, they are independent of each other;



(2)

wherein R^1 to R^6 each independently denote an alkyl group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; R^7 to R^9 each independently denote an alkylene group having 1 to 20 carbon atoms; m, n, and l each independently denote an integer of 1 to 3; (m+n+l) denotes an integer of 4 or more; and in a case that a plurality of moieties is present as any of R^1 to R^6, they are independent of each other;



(3)

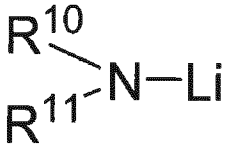
wherein R^1 to R^4 each independently denote an alkyl group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; R^5 and R^6 each independently denote an alkylene group having 1 to 20 carbon atoms; m and n each independently denote an integer of 1 to 3; (m+n) denotes an integer of 4 or more; R^7 denotes an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or a silyl group substituted with a hydrocarbon group; and in a case that a plurality of moieties is present as any of R^1 to R^4, they are independent of each other.

[Claim 10]

The method for producing the modified conjugated diene-based polymer according to claim 9, wherein the modifier comprises a modifier represented by the formula (1) with m and n therein being 2 and 3, respectively, or the modifier comprises a modifier represented by the formula (2) with each of m, n, and l therein being 3.

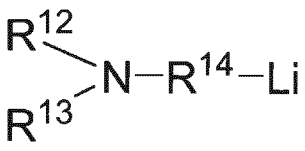
[Claim 11]

The method for producing the modified conjugated diene-based polymer according to any one of claims 8 to 10, wherein the organolithium compound comprises an organolithium compound represented by any of following general formulas (14) to (17):



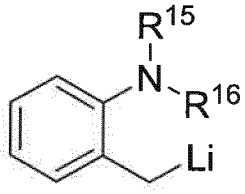
(14)

wherein R^{10} and R^{11} each independently denote at least one selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group having 3 to 14 carbon atoms, and an aralkyl group having 6 to 20 carbon atoms; R^{10} and R^{11} may be attached together to form a cyclic structure together with an adjacent nitrogen atom, and in this case, R^{10} and R^{11} denote an alkyl group having 5 to 12 carbon atoms, and may have an unsaturated bond or a branched structure in a part thereof;



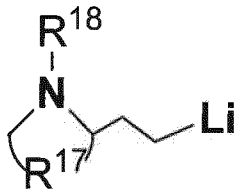
(15)

wherein R^{12} and R^{13} each independently denote at least one selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group having 3 to 14 carbon atoms, and an aralkyl group having 6 to 20 carbon atoms; R^{12} and R^{13} may be attached together to form a cyclic structure together with an adjacentnitrogen atom, and in this case, R^{12} and R^{13} denote an alkyl group having 5 to 12 carbon atoms, and may have an unsaturated bond or a branched structure in a part thereof; and R^{14} denotes an alkylene group having 1 to 20 carbon atoms or a conjugated diene-based polymer having 1 to 20 carbon atoms;



(16)

wherein R^{15} and R^{16} each independently denote at least one selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group having 3 to 14 carbon atoms, and an aryl group having 6 to 20 carbon atoms; R^{15} and R^{16} may be attached together to form a cyclic structure together with an adjacent nitrogen atom, and in this case, R^{15} and R^{16} denote an alkyl group having 5 to 12 carbon atoms, and may have a branched structure in a part thereof;



(17)

wherein R^{17} denotes a hydrocarbon group having 2 to 10 carbon atoms, and may have an unsaturated bond or a branched structure in a part thereof; and R^{18} denotes an alkyl group having 1 to 12 carbon atoms, and may have a branched structure in a part thereof.

[Claim 12]

The method for producing the modified conjugated diene-based polymer according to any one of claims 8 to 11, wherein, in the polymerization step, polymerization is performed in a continuous type, a polymerization temperature is 45°C or more and 80°C or less, and a solid content is 16% by mass or less.

[Claim 13]

The method for producing the modified conjugated diene-based polymer according to any one of claims 8 to 12, wherein, in the polymerization step, polymerization is performed in a continuous type, and a concentration of the organolithium compound is 0.010 mol/L or less based on a volume of a hydrocarbon solvent.

[Claim 14]

The method for producing the modified conjugated diene-based polymer according to any one of claims 8 to 13, wherein, in the modification step, a content of the

conjugated diene compound is 100 ppm by mass or more and 50000 ppm by mass or less based on a total amount of a monomer and a polymer.

[Claim 15]

A modified conjugated diene-based polymer obtained through the method for producing the modified conjugated diene-based polymer according to any one of claims 8 to 14.

[Claim 16]

A modified conjugated diene-based polymer composition comprising:

a rubber component and

0.5 parts by mass or more and 300 parts by mass or less of a silica-based inorganic filler based on 100 parts by mass of the rubber component,

wherein the rubber component comprises 20 parts by mass or more of the modified conjugated diene-based polymer according to any one of claims 1 to 7 and 15 based on 100 parts by mass of the rubber component.