CLAIMS

1. A method for producing a diaryl carbonate, using a metal-containing catalyst composition as a reaction catalyst, comprising:

a step (1) of subjecting a dialkyl carbonate and an aromatic monohydroxy compound to a transesterification reaction so as to obtain an alkylaryl carbonate, and removing an alcohol as by-product from a reaction system;

a step (2) of subjecting the alkylaryl carbonate obtained in the step (1) to a transesterification or disproportionation reaction so as to obtain a reaction product including the diaryl carbonate;

a step (3) of distilling the reaction product obtained in the step (2) to separate the reaction product into a low boiling component including the diaryl carbonate and a high boiling component including the reaction catalyst; and

a step (4) of recycling the high boiling component separated in the step (3) into the steps (1) and/or (2), wherein:

the high boiling component separated in the step (3) includes 70% by mass or less of a component having a higher boiling point than that of the diaryl carbonate;

the high boiling component separated in the step (3) includes a compound represented by the formula (1):

[Formula 1]

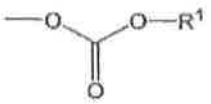


(1)

wherein Ar^1 represents an unsubstituted or substituted arylene group having 6 to

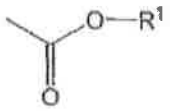
20 carbon atoms, X and Y-O are located at an ortho position to each other, X represents a hydroxy group or a substituent given by the formula (2) or (3), and Y represents hydrogen or a substituent given by the formula (3), the formulas (2) and (3) being as follows:

[Formula 2]



(2)

[Formula 3]



(3)

wherein R^1 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, an alicyclic aliphatic group having 5 to 12 carbon atoms, or an unsubstituted or substituted aryl group having 6 to 20 carbon atoms; and

after performing the method for producing the diaryl carbonate continuously in a steady state for 100 hours or more, the high boiling component recycled in the step (4) includes compounds given by (i) to (iii):

(i) a compound of the formula (1) where X represents the formula (2) or (3), and Y represents the formula (3);

(ii) a compound of the formula (1) where X represents a hydroxy group, and Y represents the formula (3), and/or a compound of the formula (1) where X represents the formula (3), and Y represents hydrogen;

(iii) a compound of the formula (1) where X represents a hydroxy group, and Y represents hydrogen;

the compounds of (i) to (iii) satisfying conditions given by (iv) to (vi), respectively:

(iv) "total moles of the compounds of (i)/moles of metal atoms" is 0.005 to 20;

(v) "total moles of the compounds of (ii)/moles of metal atoms" is 0.005 to 4; and

(vi) "moles of the compound of (iii)/moles of metal atoms" is less than 2.

2. The method for producing the diaryl carbonate according to claim 1, wherein the metal-containing catalyst composition is a titanium-containing catalyst composition.

3. The method for producing the diaryl carbonate according to claim 2, wherein the titanium-containing catalyst composition is a titanium-containing composition formed of a diaryl carbonate and an aryloxytitanium composition, and titanium constituting the aryloxytitanium composition has a content of 0.1 to 20% by mass based on 100% by mass of the titanium-containing composition.

4. The method for producing the diaryl carbonate according to claim 3, wherein the titanium constituting the aryloxytitanium composition is tetravalent.

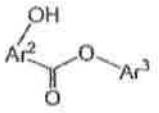
5. The method for producing the diaryl carbonate according to claim 3 or 4, wherein the aryloxytitanium composition has 1 or more and 4 or less aryloxy groups per titanium atom.

6. The method for producing the diaryl carbonate according to any one of claims 1 to 5, wherein a reaction solvent is used in the steps (1) and/or (2), and

the metal-containing catalyst composition is soluble in the reaction solvent or forms a homogeneous phase with the reaction solvent.

7. The method for producing the diaryl carbonate according to any one of claims 1 to 6, wherein the compound represented by the formula (1) is at least one selected from a group of compounds represented by the following formulas (4) to (8):

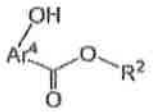
[Formula 4]



(4)

wherein Ar^2 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^3 represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and two substituents on Ar^2 are located at an ortho position to each other;

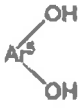
[Formula 5]



(5)

wherein Ar^4 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, R^2 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, or an alicyclic aliphatic group having 5 to 12 carbon atoms, and two substituents on Ar^4 are located at an ortho position to each other;

[Formula 6]

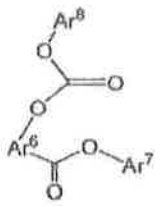


(6)

wherein Ar^5 represents an unsubstituted or substituted arylene group having 6 to

20 carbon atoms, and two hydroxy groups on Ar^5 are located at an ortho position to each other;

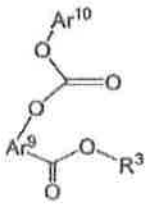
[Formula 7]



(7)

wherein Ar^6 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^7 and Ar^8 each independently represent an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and two substituents on Ar^6 are located at an ortho position to each other; and

[Formula 8]



(8)

wherein Ar^9 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^{10} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, R^3 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, or an alicyclic aliphatic group having 5 to 12 carbon atoms, and two substituents on Ar^9 are located at an ortho position to each other.

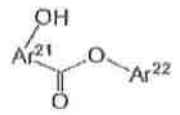
8. The method for producing the diaryl carbonate according to any one of

claims 1 to 7, wherein the high boiling component recycled in the step (4) has "total moles of the compounds represented by the formula (1)/moles of metal atoms" from 0.005 to 10.

9. The method for producing the diaryl carbonate according to any one of claims 1 to 8, wherein the steps (1) and/or (2) is performed in the presence of a composition A comprising a diaryl carbonate, an aryloxytitanium composition, and a compound represented by the following formulas (X) and/or (Y), and

the composition A has a ratio of total moles of the compounds represented by the following formulas (X) and (Y) to moles of titanium atoms (a total of the compounds represented by the formulas (X) and (Y)/titanium atoms) from 0.005 to 4, the formulas (X) and (Y) being:

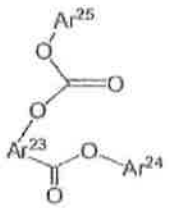
[Formula 9]



(X)

wherein Ar^{21} represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^{22} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and two substituents on Ar^{21} are located at an ortho position to each other; and

[Formula 10]



(Y)

wherein Ar^{23} represents an unsubstituted or substituted arylene group having 6 to

20 carbon atoms, Ar^{24} and Ar^{25} each independently represent an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and two substituents on Ar^{23} are located at an ortho position to each other.

10. The method for producing the diaryl carbonate according to any one of claims 1 to 9, further comprising

sampling the high boiling component recycled in the step (4),

adding a monodentate or polydentate ligand capable of coordination to the metal atoms, to the sampled high boiling component at 1 equivalent or more with respect to titanium atoms therein so as to prepare an analysis sample, and

analyzing the analysis sample to quantify the compounds given by (i) to (iii) included in the high boiling component.

11. The method for producing the diaryl carbonate according to any one of claims 1 to 10, further comprising

sampling the high boiling component recycled in the step (4),

adding at least one additive to the sampled high boiling component at 1 equivalent or more with respect to the metal atoms therein so as to prepare an analysis sample, the additive being selected from the group consisting of water, polyhydroxy compounds, nitrogen-containing heterocyclic compounds, sulfur-containing heterocyclic compounds, fluorine-substituted alcohols, and fluorine-substituted organic acids, and

analyzing the analysis sample by gas or liquid chromatography so as to quantify the compounds given by (i) to (iii) included in the high boiling component.

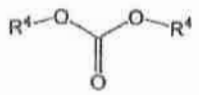
12. The method for producing the diaryl carbonate according to claim 10 or 11, further comprising

performing control so that the compounds given by (i) to (iii) included in the high boiling component recycled in the step (4) satisfy the conditions of (iv) to (vi), respectively,

after the step of quantifying the compounds given by (i) to (iii) according to claim 10 or 11.

13. The method for producing the diaryl carbonate according to any one of claims 1 to 12, wherein the dialkyl carbonate used in the step (1) is a compound represented by the formula (9):

[Formula 11]



(9)

wherein R^4 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, or an alicyclic aliphatic group having 5 to 12 carbon atoms,

the aromatic monohydroxy compound used in the step (1) is a compound represented by the formula (10):

[Formula 12]

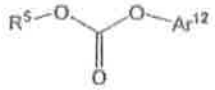


(10)

wherein Ar^{11} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms,

the alkylaryl carbonate obtained in the step (1) is a compound represented by the formula (11):

[Formula 13]

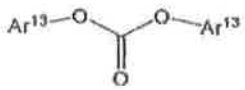


(11)

wherein R^5 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, or an alicyclic aliphatic group having 5 to 12 carbon atoms, and Ar^{12} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and

the diaryl carbonate obtained in the step (2) is a compound represented by the formula (12):

[Formula 14]



(12)

wherein Ar^{13} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms.

14. The method for producing the diaryl carbonate according to claim 9, wherein in the steps (1) and/or (2), production of the diaryl carbonate is started by feeding the composition A.

15. The method for producing the diaryl carbonate according to any one of claims 1 to 14, wherein the reactions in the steps (1) and (2) are performed using a reaction apparatus comprising at least one selected from the group consisting of an agitation tank, an agitation tank with multistage impellers, a packed column, a distillation column, a multistage distillation column, a continuous multistage distillation column, a reactor comprising an internal support, and a forced

circulation reactor.

16. The method for producing the diaryl carbonate according to claim 15, wherein in the step (1), the dialkyl carbonate and the aromatic monohydroxy compound are continuously fed to the reaction apparatus, and

in the step (2), the reaction product obtained is continuously removed from the reaction apparatus.

17. The method for producing the diaryl carbonate according to any one of claims 1 to 16, wherein the metal atoms in the metal-containing catalyst composition in the step (1) or (2) have a content of 0.0001 to 20% by mass.

18. The method for producing the diaryl carbonate according to claim 13, wherein R^4 in the formula (9) is an aliphatic alkyl group having 1 to 8 carbon atoms.

19. The method for producing the diaryl carbonate according to any one of claims 1 to 18, wherein the steps (1) and (2) have a reaction temperature of 150 to 300°C, and a reaction time of 0.05 to 50 hr.

20. The method for producing the diaryl carbonate according to any one of claims 1 to 19, wherein the distillation in the step (3) is performed by a distillation column,

the distillation column has a temperature of 150 to 300°C at a column bottom, and

the distillation column provides a residence time of 0.02 to 100 hr at a column bottom.

21. The method for producing the diaryl carbonate according to claim 3 or 4, wherein the aryloxytitanium composition is phenoxytitanium.

22. The method for producing the diaryl carbonate according to any one of claims 1 to 21, wherein the diaryl carbonate is diphenyl carbonate.

What is claimed is:

1. A method for producing a diaryl carbonate, using a metal-containing catalyst composition as a reaction catalyst, comprising:

a step (1) of subjecting a dialkyl carbonate and an aromatic monohydroxy compound to a transesterification reaction so as to obtain an alkylaryl carbonate, and removing an alcohol as by-product from a reaction system;

a step (2) of subjecting the alkylaryl carbonate obtained in the step (1) to a transesterification or disproportionation reaction so as to obtain a reaction product including the diaryl carbonate;

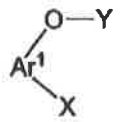
a step (3) of distilling the reaction product obtained in the step (2) to separate the reaction product into a low boiling component including the diaryl carbonate and a high boiling component including the reaction catalyst; and

a step (4) of recycling the high boiling component separated in the step (3) into the steps (1) and/or (2), wherein:

the high boiling component separated in the step (3) includes 70% by mass or less of a component having a higher boiling point than that of the diaryl carbonate;

the high boiling component separated in the step (3) includes a compound represented by the formula (1):

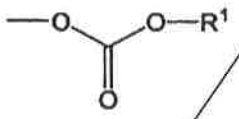
[Formula 1]



(1)

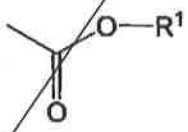
wherein Ar^1 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, X and Y-O are located at an ortho position to each other, X represents a hydroxy group or a substituent given by the formula (2) or (3), and Y represents hydrogen or a substituent given by the formula (3), the formulas (2) and (3) being as follows:

[Formula 2]



(2)

[Formula 3]



(3)

wherein R^1 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, an alicyclic aliphatic group having 5 to 12 carbon atoms, or an unsubstituted or substituted aryl group having 6 to 20 carbon atoms; and

the high boiling component recycled in the step (4) includes compounds given by (i) to (iii):

(i) a compound of the formula (1) where X represents the formula (2) or (3), and Y represents the formula (3);

(ii) a compound of the formula (1) where X represents a hydroxy group, and Y represents the formula (3), and/or a compound of the formula (1) where X represents the formula (3), and Y represents hydrogen;

(iii) a compound of the formula (1) where X represents a hydroxy group, and Y represents hydrogen;

the compounds of (i) to (iii) satisfying conditions given by (iv) to (vi), respectively:

(iv) "total moles of the compounds of (i)/moles of metal atoms" is 0.005 to 20;

(v) "total moles of the compounds of (ii)/moles of metal atoms" is 0.005 to 4; and

(vi) "moles of the compound of (iii)/moles of metal atoms" is less than 2.

2. The method for producing the diaryl carbonate according to claim 1, wherein the metal-containing catalyst composition is a titanium-containing catalyst composition.

3. The method for producing the diaryl carbonate according to claim 2, wherein the titanium-containing catalyst composition is a titanium-containing composition formed of a diaryl carbonate and an aryloxytitanium composition, and titanium constituting the aryloxytitanium composition has a content of 0.1 to 20%

by mass based on 100% by mass of the titanium-containing composition.

4. The method for producing the diaryl carbonate according to claim 3, wherein the titanium constituting the aryloxytitanium composition is tetravalent.

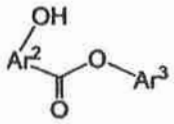
5. The method for producing the diaryl carbonate according to claim 3 or 4, wherein the aryloxytitanium composition has 1 or more and 4 or less aryloxy groups per titanium atom.

6. The method for producing the diaryl carbonate according to any one of claims 1 to 5, wherein a reaction solvent is used in the steps (1) and/or (2), and

the metal-containing catalyst composition is soluble in the reaction solvent or forms a homogeneous phase with the reaction solvent.

7. The method for producing the diaryl carbonate according to any one of claims 1 to 6, wherein the compound represented by the formula (1) is at least one selected from a group of compounds represented by the following formulas (4) to (8):

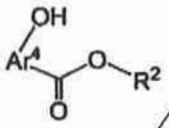
[Formula 4]



(4)

wherein Ar^2 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^3 represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and two substituents on Ar^2 are located at an ortho position to each other;

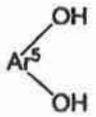
[Formula 5]



(5)

wherein Ar^4 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, R^2 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, or an alicyclic aliphatic group having 5 to 12 carbon atoms, and two substituents on Ar^4 are located at an ortho position to each other;

[Formula 6]

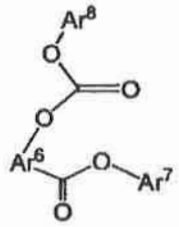


(6)

wherein Ar^5 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, and two

hydroxy groups on Ar^5 are located at an ortho position to each other;

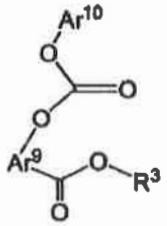
[Formula 7]



(7)

wherein Ar^6 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^7 and Ar^8 each independently represent an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and two substituents on Ar^6 are located at an ortho position to each other; and

[Formula 8]



(8)

wherein Ar^9 represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^{10} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, R^3 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, or

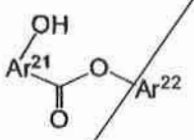
an alicyclic aliphatic group having 5 to 12 carbon atoms, and two substituents on Ar^9 are located at an ortho position to each other.

8. The method for producing the diaryl carbonate according to any one of claims 1 to 7, wherein the high boiling component recycled in the step (4) has "total moles of the compounds represented by the formula (1)/moles of metal atoms" from 0.005 to 10.

9. The method for producing the diaryl carbonate according to any one of claims 1 to 8, wherein the steps (1) and/or (2) is performed in the presence of a composition A comprising a diaryl carbonate, an aryloxytitanium composition, and a compound represented by the following formulas (X) and/or (Y), and

the composition A has a ratio of total moles of the compounds represented by the following formulas (X) and (Y) to moles of titanium atoms (a total of the compounds represented by the formulas (X) and (Y)/titanium atoms) from 0.005 to 4, the formulas (X) and (Y) being:

[Formula 9]

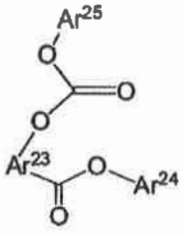


(X)

wherein Ar^{21} represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^{22}

represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and two substituents on Ar^{21} are located at an ortho position to each other; and

[Formula 10]



(Y)

wherein Ar^{23} represents an unsubstituted or substituted arylene group having 6 to 20 carbon atoms, Ar^{24} and Ar^{25} each independently represent an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and two substituents on Ar^{23} are located at an ortho position to each other.

10. The method for producing the diaryl carbonate according to any one of claims 1 to 9, further comprising

sampling the high boiling component recycled in the step (4),

adding a monodentate or polydentate ligand capable of coordination to the metal atoms, to the sampled high boiling component at 1 equivalent or more with respect to titanium atoms therein so as to prepare an analysis sample, and

analyzing the analysis sample to quantify the compounds given by (i) to (iii) included in the high boiling component.

11. The method for producing the diaryl carbonate according to any one of claims 1 to 10, further comprising

sampling the high boiling component recycled in the step (4),

adding at least one additive to the sampled high boiling component at 1 equivalent or more with respect to the metal atoms therein so as to prepare an analysis sample, the additive being selected from the group consisting of water, polyhydroxy compounds, nitrogen-containing heterocyclic compounds, sulfur-containing heterocyclic compounds, fluorine-substituted alcohols, and fluorine-substituted organic acids, and

analyzing the analysis sample by gas or liquid chromatography so as to quantify the compounds given by (i) to (iii) included in the high boiling component.

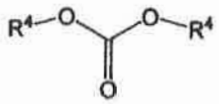
12. The method for producing the diaryl carbonate according to claim 10 or 11, further comprising

performing control so that the compounds given by (i) to (iii) included in the high boiling component recycled in the step (4) satisfy the conditions of (iv) to (vi), respectively,

after the step of quantifying the compounds given by (i) to (iii) according to claim 10 or 11.

13. The method for producing the diaryl carbonate according to any one of claims 1 to 12, wherein the dialkyl carbonate used in the step (1) is a compound represented by the formula (9):

[Formula 11]



(9)

wherein R^4 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, or an alicyclic aliphatic group having 5 to 12 carbon atoms,

the aromatic monohydroxy compound used in the step (1) is a compound represented by the formula (10):

[Formula 12]

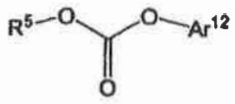


(10)

wherein Ar^{11} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms,

the alkylaryl carbonate obtained in the step (1) is a compound represented by the formula (11):

[Formula 13]

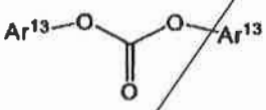


(11)

wherein R^5 represents a linear or branched aliphatic group having 1 to 12 carbon atoms, or an alicyclic aliphatic group having 5 to 12 carbon atoms, and Ar^{12} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, and

the diaryl carbonate obtained in the step (2) is a compound represented by the formula (12):

[Formula 14]



(12)

wherein Ar^{13} represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms.

14. The method for producing the diaryl carbonate according to claim 9, wherein in the steps (1) and/or (2), production of the diaryl carbonate is started by feeding the composition A.

15. The method for producing the diaryl carbonate according to any one of claims 1 to 14, wherein the reactions in the steps (1) and (2) are performed using a reaction apparatus comprising at least one selected from

the group consisting of an agitation tank, an agitation tank with multistage impellers, a packed column, a distillation column, a multistage distillation column, a continuous multistage distillation column, a reactor comprising an internal support, and a forced circulation reactor.

16. The method for producing the diaryl carbonate according to claim 15, wherein in the step (1), the dialkyl carbonate and the aromatic monohydroxy compound are continuously fed to the reaction apparatus, and

in the step (2), the reaction product obtained is continuously removed from the reaction apparatus.

17. The method for producing the diaryl carbonate according to any one of claims 1 to 16, wherein the metal atoms in the metal-containing catalyst composition in the step (1) or (2) have a content of 0.0001 to 20% by mass.

18. The method for producing the diaryl carbonate according to claim 13, wherein R^4 in the formula (9) is an aliphatic alkyl group having 1 to 8 carbon atoms.

19. The method for producing the diaryl carbonate according to any one of claims 1 to 18, wherein the steps (1) and (2) have a reaction temperature of 150 to 300°C, and a reaction time of 0.05 to 50 hr.

20. The method for producing the diaryl carbonate according to any one of claims 1 to 19, wherein the distillation in the step (3) is performed by a distillation column,

the distillation column has a temperature of 150 to 300°C at a column bottom, and

the distillation column provides a residence time of 0.02 to 100 hr at a column bottom.

21. The method for producing the diaryl carbonate according to claim 3 or 4, wherein the aryloxytitanium composition is phenoxytitanium.

22. The method for producing the diaryl carbonate according to any one of claims 1 to 21, wherein the diaryl carbonate is diphenyl carbonate.