iron of 8%. The same process as that of step (1-1) of Example 1 was carried out with the exception of supplying 1371 g (6.4 mol) of the diphenyl carbonate, 940 g (10.0 mol) of phenol and 232 g (2.0 mol) of hexamethylene diamine.

As a result of analyzing the solution following the reaction by liquid chromatography, N,N'-hexanediyl-bis-carbamic acid diphenyl ester was found to have been formed at a yield of 98.9%.

Step (14-2): Production of Isocyanate by Thermal Decomposition of N,N'-hexanediyl-bis-carbamic Acid Diphenyl Ester

The same process as that of step (1-2) of Example 1 was carried out with the exception of using the mixture obtained in step (14-1) instead of the mixture obtained in step (1-1). Liquid was continuously extracted into storage tank 809 from line 92 at the rate of about 101 g/hr. The liquid extracted from line 92 was a solution containing about 99.8% by weight of hexamethylene diisocyanate. The yield based on hexamethylene diamine was 95.2%. Although continuous operation was carried out for 10 days, there was no accumulation of adhered substances observed on the walls of thin film distillation apparatus 801.

[0133]

[Reference Example 15]

Step (15-1): Production of N,N'-hexanediyl-bis-carbamic Acid Diphenyl Ester

The diphenyl carbonate of Reference Example 1 was placed in pear-shaped flask having an internal volume of 10 L, a three-way valve, distillation column packed with Helipak No. 3, fractionating column equipped with a reflux condenser and coupled to a distillate collector, and thermometer were attached to the pear-shaped flask and the inside of the system was replaced with nitrogen in a vacuum to carry out distillative purification of the diphenyl carbonate. The flask was cooled to terminate distillative purification when distillate equal to about one-fourth the charged

amount was obtained. When ^{1}H-NMR measurement was carried out on the distillate, it was found to contain about 99.9% by weight of diphenyl carbonate. In addition, the levels of metal atoms in the form of iron, cobalt, nickel, zinc, tin, copper and titanium contained in the distillate were below the detection limit (0.001 ppm).

The same process as that of step (1-1) of Example 1 was carried out with the exception of supplying 1553 g (7.3 mol) of the diphenyl carbonate, 1175 g (12.5 mol) of phenol and 291 g (2.5 mol) of hexamethylene diamine.

As a result of analyzing the solution following the reaction by liquid chromatography, N,N'-hexanediyl-bis-carbamic acid diphenyl ester was found to have been formed at a yield of 95.6%.

Step (15-2): Production of Isocyanate by Thermal Decomposition of N,N'-hexanediyl-bis-carbamic Acid Diphenyl Ester

The same process as that of step (1-2) of Example 1 was carried out with the exception of using the mixture obtained in step (15-1) instead of the mixture obtained in step (1-1). Liquid was continuously extracted from line 92 into storage tank 809 at the rate of about 99.1 g/hr. The liquid extracted from line 92 was a solution containing about 99.8% by weight of hexamethylene diisocyanate. The yield based on hexamethylene diamine was 88.9%. Although continuous operation was carried out for 10 days, there was no accumulation of adhered substances observed on the walls of thin film distillation apparatus 801.

[0134]

[Reference Example 16]

Step (16-1): Production of N,N'-hexanediyl-bis-carbamic Acid Diphenyl Ester

Ferrous acetylacetonate was added to the diphenyl carbonate of Reference Example 1 to prepare diphenyl carbonate having a metal atom content in the form of iron of 13%. The same process as that of step (1-1) of Example 1 was carried out

CLAIMS

I (We) claim:

1. A process for producing an isocyanate, comprising the steps of:

obtaining a reaction mixture containing an aryl carbamate having an aryl group originating from a diaryl carbonate, an aromatic hydroxy compound originating from a diaryl carbonate, and a diaryl carbonate, by reacting the diaryl carbonate and an amine compound in a reaction vessel in which a reaction between the diaryl carbonate and the amine compound is carried out;

transferring the reaction mixture to a thermal decomposition reaction vessel connected by a line with the reaction vessel in which the reaction between the diaryl carbonate and the amine compound is carried out; and

obtaining the isocyanate by applying the aryl carbamate to a thermal decomposition reaction,

wherein the amine compound is a polyamine compound, and

the diaryl carbonate comprises a metal atom at from 0.001 ppm to 10%, wherein the metal atom is one kind or a plurality of kinds of the metal atoms selected from the group consisting of iron, nickel, cobalt, zinc, tin, copper and titanium atoms.

2. The process according to Claim 1, further comprising cleaning a high boiling point by-product adhered to the thermal decomposition reaction vessel, with an acid.

3. The process according to Claim 1, wherein the reaction between the diaryl carbonate and the amine compound is carried out at a stoichiometric ratio of the diaryl carbonate to amino groups constituting the amine compound being 1 or more.

4. The process according to Claim 1, wherein the diaryl carbonate and the

amine compound are reacted in the presence of an aromatic hydroxy compound as a reaction solvent.

5. The process according to Claim 4, wherein the aromatic hydroxy compound as the reaction solvent is an aromatic hydroxy compound having the same type as a compound ArOH having a structure in which a hydrogen atom is added to an ArO group constituting the diaryl carbonate ArOCOOAr (wherein Ar represents an aromatic group and O represents an oxygen atom).

6. The process according to Claim 1, wherein the reaction mixture is supplied to the thermal decomposition reaction vessel in a form of a liquid.

7. The process according to Claim 6, wherein the reaction mixture is supplied to the thermal decomposition reaction vessel while maintaining a temperature range of from 10 to 180°C.

8. The process according to Claim 1, wherein the reaction mixture is continuously supplied to the thermal decomposition reaction vessel.

9. The process according to Claim 1, wherein a low boiling point component formed in the thermal decomposition reaction is recovered from the thermal decomposition reaction vessel in a form of a gaseous phase component, and a liquid phase component is recovered from a bottom of the reaction vessel.

10. The process according to Claim 9, wherein recovery of the gaseous phase component and recovery of the liquid phase component are carried out continuously.

11. The process according to Claim 9, wherein the isocyanate obtained by a thermal decomposition reaction of the aryl carbamate is recovered from the thermal decomposition reaction vessel in a form of a gaseous phase component, and a liquid phase component containing the diaryl carbonate is recovered from the bottom of the reaction vessel.

12. The process according to Claim 11, further comprising recovering the isocyanate by distillative separation, with a distillation column, of the gaseous phase component containing the isocyanate recovered from the thermal decomposition reaction vessel, and supplying the gaseous phase component containing the isocyanate recovered from the thermal decomposition reaction vessel to the distillation column in a form of a gaseous phase.

13. The process according to Claim 11, wherein the liquid phase component containing the diaryl carbonate is a mixture containing the aryl carbamate, and all or a portion of the mixture is supplied to an upper portion of the reaction vessel.

14. The process according to Claim 9, wherein the isocyanate obtained by the thermal decomposition reaction of the aryl carbamate is recovered from the bottom of the reaction vessel in which the thermal decomposition reaction is carried out in a form of a liquid phase component.

15. The process according to Claim 14, wherein the liquid phase component recovered from the bottom of the reaction vessel comprises the isocyanate and the aryl carbamate, all or a portion of the isocyanate is separated from the liquid phase component, and all or a portion of a remainder is supplied to the upper portion of the

reaction vessel.

16. The process according to Claim 14, wherein the isocyanate is recovered by distillative separation of a mixture containing the isocyanate recovered from the thermal decomposition reaction vessel.

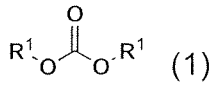
17. The process according to Claim 1, wherein a type of the reaction vessel in which the reaction between the diaryl carbonate and the amine compound is carried out and a type of the thermal decomposition reaction vessel may be the same or different, and the reaction vessel in which the reaction between the diaryl carbonate and the amine compound is carried out and the thermal decomposition reaction vessel is at least one reaction vessel selected from the group consisting of a column-type reaction vessel and a tank-type reaction vessel.

18. The process according to Claim 17, wherein the thermal decomposition reaction vessel is composed of at least one reaction vessel selected from the group consisting of an evaporator, a continuous multistage distillation column, a packed column, a thin film evaporator and a falling film evaporator.

19. The process according to Claim 1, wherein the reaction between the diaryl carbonate and the amine compound is carried out in the presence of a catalyst.

20. The process according to Claim 1, wherein the thermal decomposition reaction is carried out in a liquid phase.

21. The process according to Claim 1, wherein the diaryl carbonate is a compound represented by the following formula (1):



(1)

(wherein R^1 represents an aromatic group having 6 to 12 carbon atoms).

22. The process according to Claim 1, wherein the diaryl carbonate is a diaryl carbonate produced by a process which comprises the following steps (1) to (3):

step (1): obtaining a reaction mixture containing a dialkyl carbonate by reacting an organic tin compound having a tin-oxygen-carbon bond and carbon dioxide;

step (2): obtaining the dialkyl carbonate and a residue liquid by separating the reaction mixture; and

step (3): obtaining the diaryl carbonate by reacting the dialkyl carbonate separated in step (2) and an aromatic hydroxy compound A followed by recovering a by-product alcohol.

23. The process according to Claim 22, wherein the aromatic hydroxy compound A is an aromatic hydroxy compound having 6 to 12 carbon atoms.

24. The process according to Claim 22, wherein the diaryl carbonate is a diaryl carbonate produced by a process which further comprises the following steps

(4) and (5):

step (4): forming an organic tin compound having a tin-oxygen-carbon bond and water by reacting the residue liquid obtained in step (2) with an alcohol followed by removing the water from a reaction system; and

step (5): reusing the organic tin compound having the tin-oxygen-carbon bond obtained in step (4) as the organic tin compound having a tin-oxygen-carbon bond of step (1).

25. The process according to Claim 24, wherein the alcohol recovered in step (3) is used as all or a portion of the alcohol of the step (4).

26. The process according to Claim 9, wherein the diaryl carbonate is separated and recovered from the liquid phase component or gaseous phase component recovered from the thermal decomposition reaction vessel, and the diaryl carbonate is reused as a diaryl carbonate used as a starting material.

27. The process according to Claim 22, wherein an aromatic hydroxy compound is separated and recovered from the liquid phase component or gaseous phase component recovered from the thermal decomposition reaction, and the aromatic hydroxy compound is recycled for use as the aromatic hydroxy compound A of the step (3) or as the aromatic hydroxy compound used as the reaction solvent.

28. The process according to Claim 1, wherein the amine compound is a

compound represented by the following formula (2):

$$R^2\left(NH_2\right)_n \quad (2)$$

(wherein R^2 represents a group selected from the group consisting of an aliphatic group having 1 to 20 carbon atoms and an aromatic group having 6 to 20 carbon atoms, the above group containing an atom selected from a carbon atom and an oxygen atom, and having a valence equal to n, and

n represents an integer of from 2 to 10).

29. The process according to Claim 28, wherein the amine compound is a diamine compound in which n is 2 in the formula (2).

30. The process according to Claim 1, wherein the supply of the amine compound to the reaction vessel in which a carbonic acid ester and the amine compound are reacted is carried out in a liquid state.

31. The process according to Claim 1, wherein the supply of the amine compound to the reaction vessel in which a carbonic acid ester and the amine compound are reacted is carried out in a form of a mixture comprising an alcohol, a water or the carbonic acid ester.

~~iron of 8%. The same process as that of step (1-1) of Example 1 was carried out~~ with the exception of supplying 1371 g (6.4 mol) of the diphenyl carbonate, 940 g (10.0 mol) of phenol and 232 g (2.0 mol) of hexamethylene diamine.

As a result of analyzing the solution following the reaction by liquid chromatography, N,N'-hexanediyl-bis-carbamic acid diphenyl ester was found to have been formed at a yield of 98.9%.

Step (14-2): Production of Isocyanate by Thermal Decomposition of N,N'-hexanediyl-bis-carbamic Acid Diphenyl Ester

The same process as that of step (1-2) of Example 1 was carried out with the exception of using the mixture obtained in step (14-1) instead of the mixture obtained in step (1-1). Liquid was continuously extracted into storage tank 809 from line 92 at the rate of about 101 g/hr. The liquid extracted from line 92 was a solution containing about 99.8% by weight of hexamethylene diisocyanate. The yield based on hexamethylene diamine was 95.2%. Although continuous operation was carried out for 10 days, there was no accumulation of adhered substances observed on the walls of thin film distillation apparatus 801.

[0133]

[Example 15]

Step (15-1): Production of N,N'-hexanediyl-bis-carbamic Acid Diphenyl Ester

The diphenyl carbonate of Reference Example 1 was placed in pear-shaped flask having an internal volume of 10 L, a three-way valve, distillation column packed with Helipak No. 3, fractionating column equipped with a reflux condenser and coupled to a distillate collector, and thermometer were attached to the pear-shaped flask and the inside of the system was replaced with nitrogen in a vacuum to carry out distillative purification of the diphenyl carbonate. The flask was cooled to terminate distillative purification when distillate equal to about one-fourth the charged

amount was obtained. When ^{1}H-NMR measurement was carried out on the distillate, it was found to contain about 99.9% by weight of diphenyl carbonate. In addition, the levels of metal atoms in the form of iron, cobalt, nickel, zinc, tin, copper and titanium contained in the distillate were below the detection limit (0.001 ppm).

The same process as that of step (1-1) of Example 1 was carried out with the exception of supplying 1553 g (7.3 mol) of the diphenyl carbonate, 1175 g (12.5 mol) of phenol and 291 g (2.5 mol) of hexamethylene diamine.

As a result of analyzing the solution following the reaction by liquid chromatography, N,N'-hexanediyl-bis-carbamic acid diphenyl ester was found to have been formed at a yield of 95.6%.

Step (15-2): Production of Isocyanate by Thermal Decomposition of N,N'-hexanediyl-bis-carbamic Acid Diphenyl Ester

The same process as that of step (1-2) of Example 1 was carried out with the exception of using the mixture obtained in step (15-1) instead of the mixture obtained in step (1-1). Liquid was continuously extracted from line 92 into storage tank 809 at the rate of about 99.1 g/hr. The liquid extracted from line 92 was a solution containing about 99.8% by weight of hexamethylene diisocyanate. The yield based on hexamethylene diamine was 88.9%. Although continuous operation was carried out for 10 days, there was no accumulation of adhered substances observed on the walls of thin film distillation apparatus 801.

[0134]

[Example 16]

Step (16-1): Production of N,N'-hexanediyl-bis-carbamic Acid Diphenyl Ester

Ferrous acetylacetonate was added to the diphenyl carbonate of Reference Example 1 to prepare diphenyl carbonate having a metal atom content in the form of iron of 13%. The same process as that of step (1-1) of Example 1 was carried out

I (We) claim:

1. A process for producing an isocyanate, comprising the steps of:

obtaining a reaction mixture containing an aryl carbamate having an aryl group originating from a diaryl carbonate, an aromatic hydroxy compound originating from a diaryl carbonate, and a diaryl carbonate, by reacting the diaryl carbonate and an amine compound in a reaction vessel in which a reaction between the diaryl carbonate and the amine compound is carried out;

transferring the reaction mixture to a thermal decomposition reaction vessel connected by a line with the reaction vessel in which the reaction between the diaryl carbonate and the amine compound is carried out; and

obtaining the isocyanate by applying the aryl carbamate to a thermal decomposition reaction,

wherein the amine compound is a polyamine compound, and

the diaryl carbonate comprise a metal atom at from 0.001 ppm to 10%.

2. The process according to Claim 1, further comprising cleaning a high boiling point by-product adhered to the thermal decomposition reaction vessel, with an acid.

3. The process according to Claim 1, wherein the reaction between the diaryl carbonate and the amine compound is carried out at a stoichiometric ratio of the diaryl carbonate to amino groups constituting the amine compound being 1 or more.

4. The process according to Claim 1, wherein the diaryl carbonate and the amine compound are reacted in the presence of an aromatic hydroxy compound as a reaction solvent.

5. The process according to Claim 4, wherein the aromatic hydroxy compound as the reaction solvent is an aromatic hydroxy compound having the same type as a compound ArOH having a structure in which a hydrogen atom is added to an ArO group constituting the diaryl carbonate ArOCOOAr (wherein Ar represents an aromatic group and O represents an oxygen atom).

6. The process according to Claim 1, wherein the reaction mixture is supplied to the thermal decomposition reaction vessel in a form of a liquid.

7. The process according to Claim 6, wherein the reaction mixture is supplied to the thermal decomposition reaction vessel while maintaining a temperature range of from 10 to 180°C.

8. The process according to Claim 1, wherein the reaction mixture is continuously supplied to the thermal decomposition reaction vessel.

9. The process according to Claim 1, wherein a low boiling point component formed in the thermal decomposition reaction is recovered from the thermal decomposition reaction vessel in a form of a gaseous phase component, and a liquid phase component is recovered from a bottom of the reaction vessel.

10. The process according to Claim 9, wherein recovery of the gaseous phase component and recovery of the liquid phase component are carried out continuously.

11. The process according to Claim 9, wherein the isocyanate obtained by a

thermal decomposition reaction of the aryl carbamate is recovered from the thermal decomposition reaction vessel in a form of a gaseous phase component, and a liquid phase component containing the diaryl carbonate is recovered from the bottom of the reaction vessel.

12. The process according to Claim 11, further comprising recovering the isocyanate by distillative separation, with a distillation column, of the gaseous phase component containing the isocyanate recovered from the thermal decomposition reaction vessel, and supplying the gaseous phase component containing the isocyanate recovered from the thermal decomposition reaction vessel to the distillation column in a form of a gaseous phase.

13. The process according to Claim 11, wherein the liquid phase component containing the diaryl carbonate is a mixture containing the aryl carbamate, and all or a portion of the mixture is supplied to an upper portion of the reaction vessel.

14. The process according to Claim 9, wherein the isocyanate obtained by the thermal decomposition reaction of the aryl carbamate is recovered from the bottom of the reaction vessel in which the thermal decomposition reaction is carried out in a form of a liquid phase component.

15. The process according to Claim 14, wherein the liquid phase component recovered from the bottom of the reaction vessel comprises the isocyanate and the aryl carbamate, all or a portion of the isocyanate is separated from the liquid phase component, and all or a portion of a remainder is supplied to the upper portion of the reaction vessel.

16. The process according to Claim 14, wherein the isocyanate is recovered by distillative separation of a mixture containing the isocyanate recovered from the thermal decomposition reaction vessel.

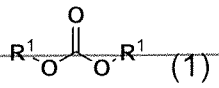
17. The process according to Claim 1, wherein a type of the reaction vessel in which the reaction between the diaryl carbonate and the amine compound is carried out and a type of the thermal decomposition reaction vessel may be the same or different, and the reaction vessel in which the reaction between the diaryl carbonate and the amine compound is carried out and the thermal decomposition reaction vessel is at least one reaction vessel selected from the group consisting of a column-type reaction vessel and a tank-type reaction vessel.

18. The process according to Claim 17, wherein the thermal decomposition reaction vessel is composed of at least one reaction vessel selected from the group consisting of an evaporator, a continuous multistage distillation column, a packed column, a thin film evaporator and a falling film evaporator.

19. The process according to Claim 1, wherein the reaction between the diaryl carbonate and the amine compound is carried out in the presence of a catalyst.

20. The process according to Claim 1, wherein the thermal decomposition reaction is carried out in a liquid phase.

21. The process according to Claim 1, wherein the diaryl carbonate is a compound represented by the following formula (1):



(1)

(wherein R^1 represents an aromatic group having 6 to 12 carbon atoms).

22. The process according to Claim 1, wherein the metal atom is one kind or a plurality of kinds of the metal atoms selected from the group consisting of iron, nickel, cobalt, zinc, tin, copper and titanium atoms.

23. The process according to Claim 1, wherein the diaryl carbonate is a diaryl carbonate produced by a process which comprises the following steps (1) to (3):

step (1): obtaining a reaction mixture containing a dialkyl carbonate by reacting an organic tin compound having a tin-oxygen-carbon bond and carbon dioxide;

step (2): obtaining the dialkyl carbonate and a residue liquid by separating the reaction mixture; and

step (3): obtaining the diaryl carbonate by reacting the dialkyl carbonate separated in step (2) and an aromatic hydroxy compound A followed by recovering a by-product alcohol.

24. The process according to Claim 23, wherein the aromatic hydroxy compound A is an aromatic hydroxy compound having 6 to 12 carbon atoms.

25. The process according to Claim 23, wherein the diaryl carbonate is a diaryl carbonate produced by a process which further comprises the following steps

(4) and (5):

step (4): forming an organic tin compound having a tin-oxygen-carbon bond and water by reacting the residue liquid obtained in step (2) with an alcohol followed by removing the water from a reaction system; and

step (5): reusing the organic tin compound having the tin-oxygen-carbon bond obtained in step (4) as the organic tin compound having a tin-oxygen-carbon bond of step (1).

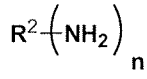
26. The process according to Claim 25, wherein the alcohol recovered in step (3) is used as all or a portion of the alcohol of the step (4).

27. The process according to Claim 9, wherein the diaryl carbonate is separated and recovered from the liquid phase component or gaseous phase component recovered from the thermal decomposition reaction vessel, and the diaryl carbonate is reused as a diaryl carbonate used as a starting material.

28. The process according to Claim 23, wherein an aromatic hydroxy compound is separated and recovered from the liquid phase component or gaseous phase component recovered from the thermal decomposition reaction, and the aromatic hydroxy compound is recycled for use as the aromatic hydroxy compound A of the step (3) or as the aromatic hydroxy compound used as the reaction solvent.

29. The process according to Claim 1, wherein the amine compound is a

compound represented by the following formula (2):



(2)

(wherein R^2 represents a group selected from the group consisting of an aliphatic group having 1 to 20 carbon atoms and an aromatic group having 6 to 20 carbon atoms, the above group containing an atom selected from a carbon atom and an oxygen atom, and having a valence equal to n, and

n represents an integer of from 2 to 10).

30. The process according to Claim 29, wherein the amine compound is a diamine compound in which n is 2 in the formula (2).

31. The process according to Claim 1, wherein the supply of the amine compound to the reaction vessel in which a carbonic acid ester and the amine compound are reacted is carried out in a liquid state.

32. The process according to Claim 1, wherein the supply of the amine compound to the reaction vessel in which a carbonic acid ester and the amine compound are reacted is carried out in a form of a mixture comprising an alcohol, a water or the carbonic acid ester.