

INDUSTRIAL PROCESS FOR PRODUCTION OF HIGH-PURITY DIARYL CARBONATE

Technical Field

5 The present invention relates to an industrial process for the production of a high-purity diaryl carbonate. More particularly, the present invention relates to an industrial process for the production of a high-purity diaryl carbonate, which is useful as a raw material of a transesterification method polycarbonate, by taking as a starting material a reaction mixture containing an alkyl aryl carbonate which has
10 been obtained through a transesterification reaction between a dialkyl carbonate and an aromatic monohydroxy compound, and carrying out a transesterification reaction using a reactive distillation column having a specified structure to obtain a diaryl carbonate, and then subjecting a reaction mixture containing the diaryl carbonate thus obtained to separation and purification using two continuous multi-stage
15 distillation columns which have specified structures.

Background Art

A high-purity diphenyl carbonate is important as a raw material for the production of an aromatic polycarbonate, which is the most widely used engineering
20 plastics, without using toxic phosgene. As a process for producing an aromatic carbonate, a process of reacting an aromatic monohydroxy compound with phosgene has been known from long ago, and has also been the subject of a variety of studies in recent years. However, this process has the problem of using phosgene, and in addition chlorinated impurities that are difficult to separate out are
25 present in the aromatic carbonate produced using this process, and hence this aromatic carbonate cannot be used as a raw material for the production of the

aromatic polycarbonate. Because such chlorinated impurities markedly inhibit the polymerization reaction in the transesterification method which is carried out in the presence of an extremely small amount of a basic catalyst; for example, even if such chlorinated impurities are present in an amount of only 1 ppm, the polymerization
5 hardly proceeds at all. To make the aromatic carbonate capable of using as a raw material of a transesterification method polycarbonate, a troublesome multi-stage separation/purification processes such as enough washing with a dilute aqueous alkaline solution and hot water, oil / water separation, distillation and so on are thus required. Furthermore, the yield of aromatic carbonate decreases due to hydrolysis
10 loss and distillation loss during this separation/purification processes. Therefore, there are many problems in carrying out this method economically on an industrial scale.

On the other hand, a process for producing aromatic carbonates through transesterification reactions between dialkyl carbonates and aromatic monohydroxy
15 compounds are also known. However, such transesterification reactions are all equilibrium reactions. Since the equilibriums are biased extremely toward the original system and the reaction rates are slow, there have been many difficulties in producing the aromatic carbonate industrially in large amounts using this method. Two types of proposals have been made to improve on the above difficulties. One
20 of these relates to development of a catalyst to increase the reaction rate, and many metal compounds have been proposed as the catalyst for the above type of the transesterification reactions. For example, Lewis acids such as transition metal halides and Lewis acid-forming compounds (see Patent Documents 1: Japanese Patent Application Laid-Open No. 51-105032, Japanese Patent Application
25 Laid-Open No. 56-123948, Japanese Patent Application Laid-Open No. 56-123949 (corresponding to West German Patent Application No. 2528412, British Patent No.

1499530, and U.S. Patent No. 4182726), Japanese Patent Application Laid-Open No. 51-75044 (corresponding to West German Patent Application No. 2552907, and U.S. Patent No. 4045464)), tin compounds such as organotin alkoxides and organotin oxides (see Patent Documents 2: Japanese Patent Application Laid-Open No. 54-48733 (corresponding to West German Patent Application No. 2736062), Japanese Patent Application Laid-Open No. 54-63023, Japanese Patent Application Laid-Open No. 60-169444 (corresponding to U.S. Patent No. 4554110), Japanese Patent Application Laid-Open No. 60-169445 (corresponding to U.S. Patent No. 4552704), Japanese Patent Application Laid-Open No. 62-277345, Japanese Patent Application Laid-Open No. 1-265063), salts and alkoxides of alkali metals and alkaline earth metals (see Patent Document 3: Japanese Patent Application Laid-Open No. 57-176932), lead compounds (see Patent Documents 4: Japanese Patent Application Laid-Open No. 57-176932, Japanese Patent Application Laid-Open No. 1-93560), complexes of metals such as copper, iron and zirconium (see Patent Document 5: Japanese Patent Application Laid-Open No. 57-183745), titanilic acid esters (see Patent Documents 6: Japanese Patent Application Laid-Open No. 58-185536 (corresponding to U.S. Patent No. 4410464), Japanese Patent Application Laid-Open No. 1-265062), mixtures of a Lewis acid and protonic acid (see Patent Document 7: Japanese Patent Application Laid-Open No. 60-173016 (corresponding to U.S. Patent No. 4609501)), compounds of Sc, Mo, Mn, Bi, Te or the like (see Patent Documents 8: Japanese Patent Application Laid-Open No. 1-265064), ferric acetate (see Patent Document 9: Japanese Patent Application Laid-Open No. 61-172852), and so on have been proposed.

Since the problem of the disadvantageous equilibrium cannot be solved merely by developing the catalyst, as the other type of the proposals, attempts have been made to devise a reaction system so as to shift the equilibrium toward the

product system as much as possible, thus improving the aromatic carbonate yield.

For example, for the reaction between dimethyl carbonate and phenol, there have been proposed a method in which methanol produced as a by-product is distilled off by azeotropy together with an azeotrope-forming agent (see Patent Documents 10:

- 5 Japanese Patent Application Laid-Open No. 54-48732 (corresponding to West German Patent Application No. 736063, and U.S. Patent No. 4252737)), and a method in which the methanol produced as a by-product is removed by being adsorbed onto a molecular sieve (see Patent Documents 11: Japanese Patent Application Laid-Open No. 58-185536 (corresponding to U.S. Patent No. 410464)).
- 10 Moreover, a method has also been proposed in which, using an apparatus in which a distillation column is provided on top of a reactor, an alcohol produced as a by-product in the reaction is separated off from the reaction mixture, and at the same time an unreacted starting material that evaporates is separated off by distillation (see Patent Documents 12: examples in Japanese Patent Application Laid-Open No.
- 15 56-123948 (corresponding to U.S. Patent No. 4182726), examples in Japanese Patent Application Laid-Open No. 56-25138, examples in Japanese Patent Application Laid-Open No. 60-169444 (corresponding to U.S. Patent No. 4554110), examples in Japanese Patent Application Laid-Open No. 60-169445 (corresponding to U.S. Patent No. 4552704), examples in Japanese Patent Application Laid-Open
- 20 No. 60-173016 (corresponding to U.S. Patent No. 4609501), examples in Japanese Patent Application Laid-Open No. 61-172852, examples in Japanese Patent Application Laid-Open No. 61-291545, examples in Japanese Patent Application Laid-Open No. 62-277345).

However, these reaction systems have basically been batch system or

25 switchover system. Because there are limitations in the improvement of the reaction rate through catalyst development for such transesterification reactions, and

the reaction rates are still slow, and thus it has been thought that the batch system is preferable to a continuous system. Of these, a continuous stirring tank reactor (CSTR) system in which a distillation column is provided on the top of the reactor has been proposed as the continuous system, but there are problems such as the
5 reaction rate being slow, and a gas-liquid interface in the reactor being small, based on the volume of the liquid. Hence it is not possible to make the reaction ratio high. Accordingly, it is difficult to attain the object of producing the aromatic carbonate continuously in large amounts stably for a prolonged period of time by means of the above-mentioned methods, and many issues remain to be resolved before
10 economical industrial implementation is possible.

The present inventors have developed reactive distillation methods in which such a transesterification reaction is carried out in a continuous multi-stage distillation column simultaneously with separation by distillation, and have been the first in the world to disclose that such a reactive distillation system is useful for such
15 a transesterification reaction, for example, a reactive distillation method in which a dialkyl carbonate and an aromatic hydroxy compound are continuously fed into the multi-stage distillation column, and the reaction is carried out continuously inside the column in which a catalyst is present, while continuously withdrawing a low boiling point component containing an alcohol produced as a by-product by distillation and
20 continuously withdrawing a component containing a produced alkyl aryl carbonate from a lower portion of the column (see Patent Document 13: Japanese Patent Application Laid-Open No. 3-291257), a reactive distillation method in which an alkyl aryl carbonate is continuously fed into the multi-stage distillation column, and the reaction is carried out continuously inside the column in which a catalyst is present,
25 while continuously withdrawing a low boiling point component containing a dialkyl carbonate produced as a by-product by distillation, and continuously withdrawing a

component containing a produced diaryl carbonate from a lower portion of the column (see Patent document 14: Japanese Patent Application Laid-Open No. 4-9358), a reactive distillation method in which these reactions are carried out using two continuous multi-stage distillation columns, and hence a diaryl carbonate is produced continuously while efficiently recycling a dialkyl carbonate produced as a by-product (see Patent document 15: Japanese Patent Application Laid-Open No. 4-211038), and a reactive distillation method in which a dialkyl carbonate and an aromatic hydroxy compound or the like are continuously fed into the multi-stage distillation column, and a liquid that flows down through the column is withdrawn from a side outlet provided at an intermediate stage and/or a lowermost stage of the distillation column, and is introduced into a reactor provided outside the distillation column so as to bring about reaction, and is then introduced back through a circulating inlet provided at a stage above the stage where the outlet is provided, whereby reaction is carried out in both the reactor and the distillation column (see Patent Documents 16: Japanese Patent Application Laid-Open No. 4-224547, Japanese Patent Application Laid-Open No. 4-230242, Japanese Patent Application Laid-Open No. 4-235951).

These reactive distillation methods proposed by the present inventors are the first to enable aromatic carbonates to be produced continuously and efficiently, and many similar reactive distillation systems based on the above disclosures have been proposed thereafter (see Patent Documents 17 to 32: Patent Document 17: International Publication No. 00/18720 (corresponding to U.S. Patent No. 5362901), Patent Document 18: Italian Patent No. 01255746, Patent Document 19: Japanese Patent Application Laid-Open No. 6-9506 (corresponding to European Patent No. 0560159, and U.S. Patent No. 5282965), Patent Document 20: Japanese Patent Application Laid-Open No. 6-41022 (corresponding to European Patent No. 0572870,

- and U.S. Patent No. 5362901), Patent Documents 21: Japanese Patent Application Laid-Open No. 6-157424 (corresponding to European Patent No. 0582931, and U.S. Patent No. 5334742), Japanese Patent Application Laid-Open No. 6-184058 (corresponding to European Patent No. 0582930, and U.S. Patent No. 5344954),
- 5 Patent Document 22: Japanese Patent Application Laid-Open No. 7-304713, Patent Document 23: Japanese Patent Application Laid-Open No. 9-40616, Patent Document 24: Japanese Patent Application Laid-Open No. 9-59225, Patent Document 25: Japanese Patent Application Laid-Open No. 9-110805, Patent Document 26: Japanese Patent Application Laid-Open No. 9-165357, Patent
- 10 Document 27: Japanese Patent Application Laid-Open No. 9-173819, Patent Documents 28: Japanese Patent Application Laid-Open No. 9-176094, Japanese Patent Application Laid-Open No. 2000-191596, Japanese Patent Application Laid-Open No. 2000-191597, Patent Documents 29: Japanese Patent Application Laid-Open No. 9-194436 (corresponding to European Patent No. 0785184, and U.S.
- 15 Patent No. 5705673), Patent Documents 30: International Publication No. 00/18720 (corresponding to U.S. Patent No. 6093842), International Publication No. 01/042187 (corresponding to Published Japanese Translation of PCT Application No. 2003-516376), Patent Documents 31: Japanese Patent Application Laid-Open No. 2001-64234, Japanese Patent Application Laid-Open No. 2001-64235, Patent
- 20 Document 32: International Publication No. 02/40439 (corresponding to U.S. Patent No. 6596894, U.S. Patent No. 6596895, and U.S. Patent No. 6600061)).

Among the reactive distillation systems, the present applicants have further proposed, as a method that enables highly pure aromatic carbonates to be produced stably for a prolonged period of time without a large amount of a catalyst being

25 required, a method in which a high boiling point material containing a catalyst component is reacted with an active substance and then separated off, and the

catalyst component is recycled (see Patent Documents 33: International Publication No. 97/11049 (corresponding to European Patent No. 0855384, and U.S. Patent No. 5872275)), and a method carried out while keeping the weight ratio of a polyhydric aromatic hydroxy compound in the reaction system to a catalyst metal at not more
5 than 2.0 (see Patent Documents 34: Japanese Patent Application Laid-Open No. 11-92429 (corresponding to European Patent No. 1016648, and U.S. Patent No. 6262210)). Furthermore, the present inventors have also proposed a method in which 70 to 99 % by weight of phenol produced as a by-product in a polymerization process is used as a starting material, and diphenyl carbonate can be produced by
10 means of the reactive distillation method. This diphenyl carbonate can be used as the raw material for polymerization to produce aromatic polycarbonates (see Patent Documents 35: Japanese Patent Application Laid-Open No. 9-255772 (corresponding to European Patent No. 0892001, and U.S. Patent No. 5747609)).

However, in all of these prior art documents in which the production of the
15 aromatic carbonates using the reactive distillation method is proposed, there is no disclosure whatsoever of a specific process or apparatus enabling mass production on an industrial scale (e.g. more than 1 ton per hr), nor is there any description suggesting such a process or apparatus. For example, the descriptions regarding heights (H_1 and H_2 : cm), diameters (D_1 and D_2 : cm), the numbers of stages (N_1 and
20 N_2), and the feeding rates of the raw materials (Q_1 and Q_2 : kg/hr) for two reactive distillation columns disclosed for producing mainly diphenyl carbonate (DPC) from dimethyl carbonate and phenol are as summarized in the following table.

TABLE 1

H ₁	D ₁	N ₁	Q ₁	H ₂	D ₂	N ₂	Q ₂	PATENT DOCUMENT
600	25	20	66	600	25	20	23	15
350	2.8	-	0.2	305	5~10	15+ PACKING	0.6	21
500	5	50	0.6	400	8	50	0.6	23
100	4	-	1.4	200	4	-	0.8	24
300	5	40	1.5	-	5	25	0.7	28
1200	20	40	86	600	25	20	31	33 34
600	-	20	66	600	-	20	22	35

In other words, the biggest continuous multi-stage distillation columns used when carrying out this reaction using the reactive distillation system are those disclosed by the present applicants in Patent Documents 33 and 34. As can be seen from Table 1, the maximum values of the various conditions for the continuous multi-stage distillation columns disclosed for the above reaction are H₁ = 1200 cm, H₂ = 600 cm, D₁ = 20 cm, D₂ = 25 cm, N₁ = N₂ = 50 (Patent Document 25), Q₁ = 86 kg/hr, and Q₂ = 31 kg/hr, and the total amount of diphenyl carbonate produced was only approximately 6.7 kg/hr, which was not an amount produced on an industrial scale.

As methods for separating the diphenyl carbonate from the reaction mixture containing a diphenyl carbonate that has been produced through transesterification reaction and the like between a dialkyl carbonate and a phenol as a starting material as described above, and then purifying the diphenyl carbonate, crystallization methods, distillation methods and the like have been proposed. With regard to the

distillation methods, three methods have been proposed. One is a method in which the diphenyl carbonate is obtained as a column top component from a distillation column; for example, there are:

I) a method in which the reaction mixture containing the catalyst is distilled as is in a batch type distillation column, and the diphenyl carbonate is obtained as the column top component (see example of Patent Document 10, example 2 of Patent Document 19);

II) a method in which the reaction mixture containing the catalyst is subjected to flash evaporation, and thus separated into a high boiling point material containing most of the catalyst and a low boiling point material, and then the low boiling point material is distilled in a distillation column for starting material recovery, and a catalyst-containing diphenyl carbonate is obtained as a column bottom material, and then this column bottom material is distilled in a purifying column, whereby the diphenyl carbonate is obtained as a column top component (see Patent Document 37: example 1 in Japanese Patent Application Laid-open No. 4-100824, Patent Document 38: Japanese Patent Application Laid-open No. 9-169704); and

III) a method in which the reaction mixture containing the catalyst is distilled in a distillation column (or evaporator), and thus separated into a high boiling point material containing most of the catalyst and a low boiling point material, and then the low boiling point material is subjected to continuous sequential distillation using a distillation apparatus comprising three columns, i.e. a light fraction separating column, a methyl phenyl carbonate separating column, and a diphenyl carbonate separating column, whereby diphenyl carbonate is obtained as a column top component (see Patent Document 25).

Another is a method in which the diphenyl carbonate is obtained as a column bottom component from a distillation column; for example, there is:

IV) a method in which the reaction mixture containing the catalyst is distilled in a distillation column, and thus separated into a high boiling point material containing most of the catalyst and a low boiling point material, and then the low boiling point material is distilled in a distillation column, and the diphenyl carbonate is
5 obtained as a column bottom component (see Patent Document 31).

The other is a method in which the diphenyl carbonate is obtained as a side cut component from a distillation column; for example, there are:

V) a method in which the reaction mixture containing the catalyst is introduced into a third reactive distillation column, and further reaction and distillation
10 are carried out, whereby the diphenyl carbonate is obtained as a side cut component from the reactive distillation column (see Patent Document 21);

VI) a method in which the reaction mixture containing the catalyst is subjected to flash evaporation, and thus separated into a high boiling point material containing most of the catalyst and a low boiling point material, and then the low
15 boiling point material is introduced into a distillation column and distillation is carried out, whereby the diphenyl carbonate is obtained as a side cut component from the reactive distillation column (see Patent Documents 34 and 35, Patent Document 39: International Publication No. 92/18458 (corresponding to U.S. Patent No. 5426207);

VII) a method in which the reaction mixture containing the catalyst is distilled
20 in a first purifying column, and thus separated into a high boiling point material containing most of the catalyst and a low boiling point material, and then the low boiling point material is introduced into a second purifying column and distillation is carried out, whereby the diphenyl carbonate is obtained as a side cut component from the second purifying column (see Patent Document 40: Japanese Patent
25 Application Laid-open No. 11-49727); and

VIII) a method in which diphenyl carbonate containing phenyl salicylate is

introduced into a distillation column having the number of theoretical stages being from 5 to 15, and distillation is carried out at a column bottom temperature of not less than 150°C, whereby the diphenyl carbonate is obtained as a side cut component from the distillation column (see Patent Document 36: Japanese Patent Application
5 Laid-open No. 9-194437 (corresponding to European Patent No. 0784048)).

However, it has been shown that various problems remain with such diphenyl carbonate separation/purification methods using these distillations. More specifically, the purity of the diphenyl carbonate obtained through the above I) is low, and moreover this is a batch process and hence is not suitable for mass production
10 on an industrial scale. Regarding the above II), the method of Patent Document 37 is a batch method, and the diphenyl carbonate which was obtained through the method disclosed in Patent Document 38 contains a titanium catalyst, albeit in an amount of not more than 1 ppm, and hence is not suitable as a raw material for the production of a high-purity discolored polycarbonate. With the method of the above
15 III), since the diphenyl carbonate is heated to a high temperature at the bottom of each of two of the distillation columns, i.e. the light fraction separating column and the methyl phenyl carbonate separating column, and is then subjected to a high temperature in the diphenyl carbonate separating column, the diphenyl carbonate is altered, bringing about a decrease in the purity and a decrease in the yield.

20 Moreover, the method of the above IV) in which the diphenyl carbonate is obtained from the column bottom is unsuitable, because the purity is low and hence a desired polycarbonate cannot be produced.

With the method of the above V), the reaction mixture containing the catalyst, the unreacted starting material and the impurities obtained from the bottom of the
25 second reactive distillation column is introduced into the third reactive distillation column from an upper portion thereof, and the diphenyl carbonate is withdrawn from

the side of the third reactive distillation column. Vapor or mist of the catalyst, the starting material, the impurities and the like may thus be entrained, and hence the purity of the diphenyl carbonate is low. With the method of the above VI), the amount of diphenyl carbonate produced is 6.7 kg/hr (example 3 of Patent Document 34) or 3.9 kg/hr (example 1 of Patent Document 35), which is not on an industrial scale. The method of the above VII) is a preferable process, but the amount of diphenyl carbonate produced is small at 2 kg/hr (example 8 of Patent Document 40), which is not on an industrial scale. Moreover, the method is carried out with the column top pressure in the first purifying column at a high vacuum of 200 Pa, and hence industrial implementation would be difficult, because a very large distillation column would be required so that the high vacuum could be maintained.

Moreover, with the method of the above VIII), although it is stated that the content of phenyl salicylate is reduced from 3000 ppm to 50 ppm (example 2 of Patent Document 36), nothing is stated whatsoever for other impurities. For example, even though the diphenyl carbonate is produced using the phosgene method in this example, and hence this is definitely a purification method for diphenyl carbonate containing chlorinated impurities, nothing is stated whatsoever with regard to the chlorinated impurities (which have an adverse effect on the polymerization to produce a polycarbonate and the properties of the polycarbonate even in an extremely small amount of only a few tens of ppb). With this method, such chlorinated impurities will not be separated out sufficiently, and hence it will not be possible to use the diphenyl carbonate as a raw material for a polycarbonate. This is as described in comparative example 1 (in which the alkali column is not used) of the purification method (in which after washing twice with alkaline hot water, washing with hot water is carried out, and then the diphenyl carbonate is dehydrated through distillation and then passed through a column filled with a solid alkali, before being

subjected to reduced pressure distillation in the multi-stage distillation column) of Patent Document 41 (Japanese Patent Application Laid-Open No. 9-194437), which was filed more than one year after the filing of Patent Document 36.

Furthermore, in Patent Document 36, the temperature and time at which phenol starts to be distilled off in the case that reaction is carried out with bisphenol A are given as a method of evaluating the purity of the diphenyl carbonate obtained through the distillation, but evaluation of whether the diphenyl carbonate is suitable for polymerization cannot be carried out using this test method. This is because even for diphenyl carbonate of low purity such that a polycarbonate of the required degree of polymerization cannot be produced, the initial reaction in which phenol is eliminated occurs sufficiently. Moreover, since with this evaluation method, a large amount of 2.3 ppm of NaOH based on the bisphenol A is used as a catalyst, even for diphenyl carbonate containing, for example, 1 ppm of chlorinated impurities, an incorrect evaluation that the diphenyl carbonate is of high purity and is suitable as a raw material for a polycarbonate would be obtained. As stated earlier, the diphenyl carbonate containing 1 ppm of chlorinated impurities cannot be used as the raw material for the polycarbonate at all. In ordinary polymerization, since such a large amount of an alkaline catalyst is not used, this evaluation method is not suitable for evaluating the purity of diphenyl carbonate to be used for producing polycarbonate. Further, in Patent Document 36, there is no specific description whatsoever of purification of diphenyl carbonate that has been obtained using the transesterification method. Since the types and contents of impurities differ between diphenyl carbonate obtained through the phosgene method and diphenyl carbonate obtained using the transesterification method, it cannot be said that diphenyl carbonate of the same purity will be obtained through the same purification method. It thus cannot be said at all that diphenyl carbonate having the required purity for the raw material

of the polycarbonate would be obtained through the purification method of Patent Document 36. Furthermore, the amount of purified diphenyl carbonate disclosed in Patent Document 36 is 0.57 kg/hr, which is not on an industrial scale.

A reaction mixture obtained through transesterification reaction between a
5 dialkyl carbonate and a phenol as a starting material in the presence of a
homogeneous catalyst generally contains various reaction by-products. In particular,
if a diphenyl carbonate containing the amounts of high boiling point by-products
having a higher boiling point than that of the diphenyl carbonate, such as phenyl
salicylate, xanthone, phenyl methoxybenzoate,
10 1-phenoxy carbonyl-2-phenoxy carboxy-phenylene and the like which have not been
reduced down to a sufficient level is used as the raw material of the
transesterification method polycarbonate, then these high boiling point by-products
will cause coloration and deterioration in properties. It is thus preferable to reduce
the amounts of such impurities as much as possible. However, such high boiling
15 point by-products are difficult to separate out, and with methods proposed hitherto, it
has not been possible to reduce the amounts of such high boiling point by-products
down to a sufficient level. In particular, there has been no proposal whatsoever of a
process for the production on an industrial scale of not less than 1 ton / hr of a
high-purity diphenyl carbonate required for the raw material of a high-quality and
20 high-performance polycarbonate.

Disclosure of Invention

It is an object of the present invention to provide a specific process which
enables a high-purity diaryl carbonate that can be used as a raw material of a
25 high-quality and high-performance polycarbonate to be produced stably for a
prolonged period of time on an industrial scale of not less than 1 ton / hr using as a

starting material a reaction mixture containing an alkyl aryl carbonate obtained through a transesterification reaction between a dialkyl carbonate and an aromatic monohydroxy compound.

Since the present inventors disclosed a process for producing aromatic carbonates using the continuous multi-stage distillation column, various proposals regarding processes for the production of reaction mixtures containing aromatic carbonates by means of the reactive distillation method have been made. However, these have all been on a small scale and a short operating time laboratory level, and there have been no disclosures on a specific process or apparatus enabling mass production on an industrial scale from such a reaction mixture to a high-purity diaryl carbonate that can be used as the raw material of a high-quality and high-performance polycarbonate. In view of these circumstances, the present inventors carried out studies aimed at discovering a specific process enabling a high-purity diaryl carbonate which is important as the raw material of the high-quality and high-performance polycarbonate to be produced stably for a prolonged period of time on an industrial scale of not less than 1 ton / hr. As a result, the present inventors have reached to the present invention.

That is, in the first aspect of the present invention, there is provided:

1. In an industrial process for the production of a high-purity diaryl carbonate in which the high-purity diaryl carbonate is produced by taking as a starting material a reaction mixture containing an alkyl aryl carbonate, which has been obtained through a transesterification reaction between a dialkyl carbonate and an aromatic monohydroxy compound, continuously feeding the starting material into a reactive distillation column comprising a continuous multi-stage distillation column in which a homogeneous catalyst is present, carrying out a transesterification reaction and distillation simultaneously in the column, continuously withdrawing a low boiling point

reaction mixture containing a produced dialkyl carbonate from an upper portion of the column in a gaseous form, and continuously withdrawing a high boiling point reaction mixture containing a diaryl carbonate from a lower portion of the column in a liquid form, continuously introducing said high boiling point reaction mixture into a high boiling point material separating column A, and continuously carrying out separation by distillation into a column top component A_T containing the diaryl carbonate and a column bottom component A_B containing the catalyst, and then continuously introducing the column top component A_T into a diaryl carbonate purifying column B having a side cut outlet, and continuously carrying out separation by distillation into a column top component B_T , a side cut component B_S and a column bottom component B_B , the improvement which comprises:

(a) said reactive distillation column comprises a continuous multi-stage distillation column having a length L (cm), an inside diameter D (cm), an internal with a number of stages n thereinside, a gas outlet having an inside diameter d_1 (cm) at the top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_2 (cm) at the bottom of the column or in a lower portion of the column near to the bottom, at least one inlet provided in the upper portion and/or a middle portion of the column below the gas outlet, and at least one inlet provided in the lower portion of the column above the liquid outlet, wherein L , D , n , d_1 , and d_2 satisfy the following formulae (1) to (6);

$$1500 \leq L \leq 8000 \quad (1)$$

$$100 \leq D \leq 2000 \quad (2)$$

$$2 \leq L/D \leq 40 \quad (3)$$

$$10 \leq n \leq 80 \quad (4)$$

$$2 \leq D/d_1 \leq 15 \quad (5)$$

$$5 \leq D/d_2 \leq 30 \quad (6);$$

(b) said high boiling point material separating column A comprises a continuous multi-stage distillation column having a length L_A (cm), an inside diameter D_A (cm), and an internal with a number of stages n_A thereinside, wherein L_A , D_A , and n_A satisfy the following formulae (7) to (9);

$$800 \leq L_A \leq 3000 \quad (7)$$

$$100 \leq D_A \leq 1000 \quad (8)$$

$$20 \leq n_A \leq 100 \quad (9);$$

(c) said diaryl carbonate purifying column B comprises a continuous multi-stage distillation column having a length L_B (cm), an inside diameter D_B (cm), an internal thereinside, an inlet B1 at an intermediate portion of the column, and a side cut outlet B2 between the inlet B1 and the column bottom, in which a number of stages of the internal above the inlet B1 is n_1 , a number of stages of the internals between the inlet B1 and the side cut outlet B2 is n_2 , a number of stages of the internals below the side cut outlet B2 is n_3 , and a total number of stages is $n_B (= n_1 + n_2 + n_3)$, wherein L_B , D_B , n_1 , n_2 , n_3 , and n_B satisfy the following formulae (10) to (15);

$$1000 \leq L_B \leq 5000 \quad (10)$$

$$100 \leq D_B \leq 1000 \quad (11)$$

$$5 \leq n_1 \leq 20 \quad (12)$$

$$12 \leq n_2 \leq 40 \quad (13)$$

$$3 \leq n_3 \leq 15 \quad (14)$$

$$20 \leq n_B \leq 70 \quad (15); \text{ and}$$

(d) not less than 1 ton / hr of the high-purity diaryl carbonate is obtained continuously as the side cut component B_s .

2. The process according to item 1, wherein a distillation operation of said high boiling point material separating column A is carried out at a column bottom temperature T_A in a range of from 185 to 280°C, and at a column top pressure P_A in

a range of from 1000 to 20000 Pa, and a distillation operation of said diaryl carbonate purifying column B is carried out at a column bottom temperature T_B in a range of from 185 to 280°C, and at a column top pressure P_B in a range of from 1000 to 20000 Pa.

- 5 3. The process according to item 1 or 2, wherein L , D , L/D , and n for said reactive distillation column satisfy the following formulae; $2000 \leq L \leq 6000$, $150 \leq D \leq 1000$, $3 \leq L/D \leq 30$, and $15 \leq n \leq 60$, respectively,

L_A , D_A , and n_A for said high boiling point material separating column A satisfy the following formulae; $1000 \leq L_A \leq 2500$, $200 \leq D_A \leq 600$, and $30 \leq n_A \leq$
10 70, respectively,

L_B , D_B , n_1 , n_2 , n_3 , and n_B for said diaryl carbonate purifying column B satisfy the following formulae; $1500 \leq L_B \leq 3000$, $150 \leq D_B \leq 500$, $7 \leq n_1 \leq 15$, $12 \leq n_2 \leq 30$, $3 \leq n_3 \leq 10$, and $25 \leq n_B \leq 55$, respectively,

T_A is in a range of from 190 to 240°C, P_A is in a range of from 2000 to 15000
15 Pa, T_B is in a range of from 190 to 240°C, and P_B is in a range of from 2000 to 15000 Pa.

4. The process according to any one of items 1 to 3, wherein each of said reactive distillation column, said high boiling point material separating column A and said diaryl carbonate purifying column B is a distillation column having a tray and/or a
20 packing as said internal.

5. The process according to any one of items 1 to 4, wherein said reactive distillation column is a distillation column having, as the internal, the packing in the upper portion of the column, and the tray in the lower portion of the column, and the internal of each of said high boiling point material separating column A and said
25 diaryl carbonate purifying column B is the packing.

6. The process according to item 5, wherein the packing is a structured packing

which is at least one selected from the group consisting of Mellapak, Gempak, TECHNO-PAK, FLEXI-PAK, a Sulzer packing, a Goodroll packing, and a Glitchgrid.

7. The process according to item 4 or 5, wherein said tray of said reactive distillation column is a sieve tray having a sieve portion and a down comer portion.

5 8. The process according to item 7, wherein said sieve tray has 100 to 1000 holes / m^2 in the sieve portion.

9. The process according to item 7 or 8, wherein the cross-sectional area per hole of said sieve tray is in a range of from 0.5 to 5 cm^2 .

In the second aspect of the present invention, there is provided:

10 10. A high-purity diphenyl carbonate which is a diaryl carbonate produced by the process according to any one of claims 1 to 9, said diphenyl carbonate being unsubstituted or substituted with a lower hydrocarbon, and having a halogen content of not more than 0.1 ppm, and a content of by-products having a higher boiling point than that of said diphenyl carbonate of not more than 100 ppm.

15 11. The high-purity diphenyl carbonate according to item 10, wherein said diphenyl carbonate is unsubstituted diphenyl carbonate, and the halogen content is not more than 10 ppb, and the content of each of phenyl salicylate, xanthone, phenyl methoxybenzoate, and 1-phenoxy carbonyl-2-phenoxy carboxy-phenylene, which are the by-products having the higher boiling point than that of the diphenyl carbonate, is
20 not more than 30 ppm.

12. The high-purity diphenyl carbonate according to item 11, wherein the content of the by-products having the higher boiling point than that of the diphenyl carbonate is not more than 50 ppm.

13. The high-purity diphenyl carbonate according to item 12, wherein the halogen
25 content is not more than 1 ppb, and the content of the by-products having the higher boiling point than that of the diphenyl carbonate is not more than 10 ppm.

In the third aspect of the present invention, there is provided:

14. An apparatus for producing a high-purity diaryl carbonate which comprises;

a reactive distillation column comprising a continuous multi-stage distillation column in which a homogeneous catalyst is present, said reactive distillation column
5 receiving a reaction mixture containing an alkyl aryl carbonate as a starting material, which has been obtained through a transesterification reaction between a dialkyl carbonate and an aromatic monohydroxy compound, wherein a transesterification reaction and distillation simultaneously is carried out in the column, a low boiling point reaction mixture containing a produced dialkyl carbonate is withdrawn from an
10 upper portion of the column in a gaseous form, and a high boiling point reaction mixture containing a diaryl carbonate is withdrawn from a lower portion of the column in a liquid form;

a high boiling point material separating column A connected with said reactive distillation column and receiving said high boiling point reaction mixture,
15 wherein separation and distillation is carried out into a column top component A_T containing the diaryl carbonate and a column bottom component A_B containing the catalyst; and

a diaryl carbonate purifying column B which is provided with a side cut outlet, and which is connected with said high boiling point material separating column A and
20 receiving the column top component A_T from the side cut outlet, wherein separation and distillation is carried out into a column top component B_T , a side cut component B_S and a column bottom component B_B ; wherein

(a) said reactive distillation column comprises a continuous multi-stage distillation column having a length L (cm), an inside diameter D (cm), an internal with
25 a number of stages n thereinside, a gas outlet having an inside diameter d_1 (cm) at the top of the column or in an upper portion of the column near to the top, a liquid

outlet having an inside diameter d_2 (cm) at the bottom of the column or in a lower portion of the column near to the bottom, at least one inlet provided in the upper portion and/or a middle portion of the column below the gas outlet, and at least one inlet provided in the lower portion of the column above the liquid outlet, wherein L , D ,

5 n , d_1 , and d_2 satisfy the following formulae (1) to (6);

$$1500 \leq L \leq 8000 \quad (1)$$

$$100 \leq D \leq 2000 \quad (2)$$

$$2 \leq L / D \leq 40 \quad (3)$$

$$10 \leq n \leq 80 \quad (4)$$

10 $2 \leq D / d_1 \leq 15 \quad (5)$

$$5 \leq D / d_2 \leq 30 \quad (6);$$

(b) said high boiling point material separating column A comprises a continuous multi-stage distillation column having a length L_A (cm), an inside diameter D_A (cm), and an internal with a number of stages n_A thereinside, wherein L_A , D_A , and

15 n_A satisfy the following formulae (7) to (9);

$$800 \leq L_A \leq 3000 \quad (7)$$

$$100 \leq D_A \leq 1000 \quad (8)$$

$$20 \leq n_A \leq 100 \quad (9);$$

(c) said diaryl carbonate purifying column B comprises a continuous
20 multi-stage distillation column having a length L_B (cm), an inside diameter D_B (cm), an internal thereinside, an inlet B1 at an intermediate portion of the column, and a side cut outlet B2 between the inlet B1 and the column bottom, in which a number of stages of the internal above the inlet B1 is n_1 , a number of stages of the internals between the inlet B1 and the side cut outlet B2 is n_2 , a number of stages of the
25 internals below the side cut outlet B2 is n_3 , and a total number of stages is $n_B (= n_1 + n_2 + n_3)$, wherein L_B , D_B , n_1 , n_2 , n_3 , and n_B satisfy the following formulae (10) to (15);

$$1000 \leq L_B \leq 5000 \quad (10)$$

$$100 \leq D_B \leq 1000 \quad (11)$$

$$5 \leq n_1 \leq 20 \quad (12)$$

$$12 \leq n_2 \leq 40 \quad (13)$$

$$5 \quad 3 \leq n_3 \leq 15 \quad (14)$$

$$20 \leq n_B \leq 70 \quad (15).$$

15. The apparatus according to item 14, wherein a distillation operation of said high boiling point material separating column A is carried out at a column bottom temperature T_A in a range of from 185 to 280°C, and at a column top pressure P_A in a range of from 1000 to 20000 Pa, and a distillation operation of said diaryl carbonate purifying column B is carried out at a column bottom temperature T_B in a range of from 185 to 280°C, and at a column top pressure P_B in a range of from 1000 to 20000 Pa.

16. The apparatus according to item 14 or 15, wherein L , D , L/D , and n for said reactive distillation column satisfy the following formulae; $2000 \leq L \leq 6000$, $150 \leq D \leq 1000$, $3 \leq L/D \leq 30$, and $15 \leq n \leq 60$, respectively,

L_A , D_A , and n_A for said high boiling point material separating column A satisfy the following formulae; $1000 \leq L_A \leq 2500$, $200 \leq D_A \leq 600$, and $30 \leq n_A \leq 70$, respectively,

20 L_B , D_B , n_1 , n_2 , n_3 , and n_B for said diaryl carbonate purifying column B satisfy the following formulae; $1500 \leq L_B \leq 3000$, $150 \leq D_B \leq 500$, $7 \leq n_1 \leq 15$, $12 \leq n_2 \leq 30$, $3 \leq n_3 \leq 10$, and $25 \leq n_B \leq 55$, respectively,

T_A is in a range of from 190 to 240°C, P_A is in a range of from 2000 to 15000 Pa, T_B is in a range of from 190 to 240°C, and P_B is in a range of from 2000 to 15000 Pa.

17. The apparatus according to any one of items 14 to 16, wherein each of said

reactive distillation column, said high boiling point material separating column A and said diaryl carbonate purifying column B is a distillation column having a tray and/or a packing as said internal.

18. The apparatus according to any one of items 14 to 17, wherein said reactive
5 distillation column is a distillation column having, as the internal, the packing in the upper portion of the column, and the tray in the lower portion of the column, and the internal of each of said high boiling point material separating column A and said diaryl carbonate purifying column B is the packing.

19. The apparatus according to item 18, wherein the packing is a structured
10 packing which is at least one selected from the group consisting of Mellapak, Gempak, TECHNO-PAK, FLEXI-PAK, a Sulzer packing, a Goodroll packing, and a Glitchgrid.

20. The apparatus according to item 17 or 18, wherein said tray of said reactive distillation column is a sieve tray having a sieve portion and a down comer portion.

21. The apparatus according to item 20, wherein said sieve tray has 100 to 1000
15 holes / m² in the sieve portion.

22. The apparatus according to item 20 or 21, wherein the cross-sectional area per hole of said sieve tray is in a range of from 0.5 to 5 cm².

20 Advantageous Effect of the Invention

It has been discovered that by implementing the present invention, a high-purity diaryl carbonate that can be used as a raw material of a high-quality and high-performance polycarbonate can be produced on an industrial scale of not less than 1 ton / hr, preferably not less than 2 ton / hr, more preferably not less than 3 ton
25 / hr, stably for a prolonged period of time of not less than 2000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours, from a reaction

mixture containing an alkyl aryl carbonate that has been obtained through a transesterification reaction between a dialkyl carbonate and an aromatic monohydroxy compound.

5 Brief Description of Drawings

FIG. 1 is a schematic view of an example showing a reactive distillation column for carrying out the present invention; and

FIG. 2 is a schematic view of an example showing a continuous separating /
purifying apparatus for carrying out the present invention in which a high boiling point
10 material separating column A and a diaryl carbonate purifying column B are
connected together. As one example, each of these continuous multi-stage
distillation columns has installed therein an internal comprising a structured packing
having a predetermined number of stages.

1: gas outlet; 2: liquid outlet; 3 and 4: inlet; 5: end plate; 6: internal; L: length of trunk
15 portion (cm); D: inside diameter of trunk portion (cm); d_1 : inside diameter of gas
outlet (cm); d_2 : inside diameter of liquid outlet (cm); A1 and B1: inlet; B2: outlet; 11:
outlet for a column bottom component of high boiling point material column A; 13 and
23: column top gas outlet; 14, 24, 18, 28, and 38: heat exchanger; 15 and 25: reflux
liquid inlet; 16: outlet for a column top component of high boiling point material
20 column A; 17 and 27: column bottom liquid outlet; 26: outlet for a column top
component of diaryl carbonate purifying column B; 31: outlet for a column bottom
component of diaryl carbonate purifying column B; 33: outlet for a side cut
component of diaryl carbonate purifying column B.

25 Best Mode for Carrying out the Invention

In the following, the present invention is described in detail.

A dialkyl carbonate used in the present invention is a compound represented by the general formula (16);



wherein R^1 represents an alkyl group having 1 to 10 carbon atoms, an alicyclic group having 3 to 10 carbon atoms, or an aralkyl group having 6 to 10 carbon atoms.

Examples of R^1 include an alkyl group such as methyl, ethyl, propyl (isomers), allyl, butyl (isomers), butenyl (isomers), pentyl (isomers), hexyl (isomers), heptyl (isomers), octyl (isomers), nonyl (isomers), decyl (isomers) and cyclohexylmethyl; an alicyclic group such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl; and an aralkyl group such as benzyl, phenethyl (isomers), phenylpropyl (isomers), phenylbutyl (isomers) and methylbenzyl (isomers). The above-mentioned alkyl groups, alicyclic group and aralkyl group may be substituted with other substituents such as a lower alkyl group, a lower alkoxy group, a cyano group or a halogen atom, and may also contain an unsaturated bond therein.

Examples of dialkyl carbonates having such R^1 include dimethyl carbonate, diethyl carbonate, dipropyl carbonate (isomers), diallyl carbonate, dibutenyl carbonate (isomers), dibutyl carbonate (isomers), dipentyl carbonate (isomers), dihexyl carbonate (isomers), diheptyl carbonate (isomers), dioctyl carbonate (isomers), dinonyl carbonate (isomers), didecyl carbonate (isomers), dicyclopentyl carbonate, dicyclohexyl carbonate, dicycloheptyl carbonate, dibenzyl carbonate, diphenethyl carbonate (isomers), di(phenylpropyl) carbonate (isomers), di(phenylbutyl) carbonate (isomers), di(chlorobenzyl) carbonate (isomers), di(methoxybenzyl) carbonate (isomers), di(methoxymethyl) carbonate, di(methoxyethyl) carbonate (isomers), di(chloroethyl) carbonate (isomers) and di(cyanoethyl) carbonate (isomers).

Of these dialkyl carbonates, ones preferably used in the present invention

are dialkyl carbonates in which R^1 is an alkyl group having not more than four carbon atoms and not containing a halogen atom. A particularly preferable one is dimethyl carbonate. Moreover, of preferable dialkyl carbonates, particularly preferable ones are dialkyl carbonates produced in a state substantially not containing a halogen, for example ones produced from an alkylene carbonate substantially not containing a halogen and an alcohol substantially not containing a halogen.

An aromatic monohydroxy compound used in the present invention is a compound represented by the following formula (17). The type of the aromatic monohydroxy compound is not limited, so long as the hydroxyl group is directly bonded to the aromatic group;



wherein Ar^1 represents an aromatic group having 5 to 30 carbon atoms. Examples of aromatic monohydroxy compounds having such Ar^1 include phenol; various alkylphenols such as cresol (isomers), xlenol (isomers), trimethylphenol (isomers), tetramethylphenol (isomers), ethylphenol (isomers), propylphenol (isomers), butylphenol (isomers), diethylphenol (isomers), methylethylphenol (isomers), methylpropylphenol (isomers), dipropylphenol (isomers), methylbutylphenol (isomers), pentylphenol (isomers), hexylphenol (isomers) and cyclohexylphenol (isomers); various alkoxyphenols such as methoxyphenol (isomers) and ethoxyphenol (isomers); arylalkylphenols such as phenylpropylphenol (isomers); naphthol (isomers) and various substituted naphthols; and heteroaromatic monohydroxy compounds such as hydroxypyridine (isomers), hydroxycoumarin (isomers) and hydroxyquinoline (isomers). Of these aromatic monohydroxy compounds, ones preferably used in the present invention are unsubstituted and substituted phenols in which Ar^1 is an aromatic group having 6 to 10 carbon atoms. Phenol is particularly preferable. Moreover, of these aromatic monohydroxy

compounds, ones substantially not containing a halogen are preferably used in the present invention.

The molar ratio of the dialkyl carbonate to the aromatic monohydroxy compound used for obtaining a reaction mixture containing an alkyl aryl carbonate that is the starting material in the present invention must be in a range of from 0.5 to 3. Outside this range, the amount of unreacted material remaining relative to the required amount of the alkyl aryl carbonate aimed for becomes high, which is not efficient, and moreover much energy is required to recover the alkyl aryl carbonate. For such reasons, the above molar ratio is more preferably in a range of from 0.5 to 5, yet more preferably from 1 to 3.

A catalyst used in the present invention is a homogeneous catalyst which contains a metal such as Pb, Cu, Zn, Fe, Co, Ni, Al, Ti, V, Sn and the like, and which dissolves in the reaction system. A catalyst in which such a metallic component is bonded to organic groups can thus be preferably used. The catalyst component may of course have been reacted with an organic compound present in the reaction system such as aliphatic alcohols, aromatic monohydroxy compounds, alkyl aryl carbonates, diaryl carbonates or dialkyl carbonates, or may have been subjected to heating treatment with the starting material or products prior to the reaction. The catalyst used in the present invention is preferably one that has a high solubility in the reaction liquid under the reaction conditions. Examples of preferable catalysts in this sense include PbO, Pb(OH)₂ and Pb(OPh)₂; TiCl₄, Ti(OMe)₄, (MeO)Ti(OPh)₃, (MeO)₂Ti(OPh)₂, (MeO)₃Ti(OPh) and Ti(OPh)₄; SnCl₄, Sn(OPh)₄, Bu₂SnO and Bu₂Sn(OPh)₂; FeCl₃, Fe(OH)₃ and Fe(OPh)₃; and such catalysts that have been treated with phenol, the reaction liquid and the like.

In the present invention, it is particularly preferable to use a starting material and catalyst not containing a halogen. In this case, the diaryl carbonate produced

does not contain a halogen at all, and hence it is important as a raw material when industrially producing a polycarbonate by means of a transesterification method.

The reason is that even if a halogen is present in the raw material for the polymerization in even an amount less than, for example, 1 ppm, then this halogen
5 does inhibit the polymerization reaction, and cause a deterioration in the properties of the polycarbonate produced, and cause discoloration of the polycarbonate.

The process for the production of the reaction mixture containing the alkyl aryl carbonate obtained through a transesterification reaction between the dialkyl carbonate and the aromatic monohydroxy compound may be any process, but one
10 particularly preferable for industrial implementation is a process in which a continuous multi-stage distillation column is used as a reactive distillation column as previously proposed by the present inventors. A particularly preferable such process is one in which the transesterification reaction between the dialkyl carbonate and the aromatic monohydroxy compound is carried out in the presence of a
15 homogeneous catalyst, and a reaction mixture containing an alcohol is continuously withdrawn from the top of the column, while the reaction mixture containing the alkyl aryl carbonate is continuously withdrawn from the bottom of the column.

In the present invention, the reaction mixture containing the alkyl aryl carbonate obtained in this way is continuously fed into a reactive distillation column
20 comprising a continuous multi-stage distillation column in which a homogeneous catalyst is present, a transesterification reaction and distillation are carried out simultaneously in the column, a low boiling point reaction mixture containing a produced dialkyl carbonate is continuously withdrawn from an upper portion of the column in a gaseous form, and a high boiling point reaction mixture containing a
25 diaryl carbonate is continuously withdrawn from a lower portion of the column in a liquid form. Included under the transesterification reaction are a reaction in which

the alkoxy group of the alkyl aryl carbonate is exchanged with the aryloxy group of the aromatic monohydroxy compound present in the system and an alcohol is eliminated, and a reaction in which two molecules of the alkyl aryl carbonate are converted into the diaryl carbonate and the dialkyl carbonate through a

5 transesterification reaction therebetween, i.e. a disproportionation reaction. In the reactive distillation column in the present invention, it is mainly the disproportionation reaction of the alkyl aryl carbonate that occurs.

The reaction mixture containing the alkyl aryl carbonate used as the starting material in the present invention may be of high purity, or may contain other
10 compounds, for example may contain the dialkyl carbonate and/or the aromatic monohydroxy compound used for obtaining the alkyl aryl carbonate, or may contain compounds or reaction by-products produced in this process and/or another process, for example an alcohol, an alkyl aryl ether, and/or the diaryl carbonate. A method in which the reaction mixture obtained through the transesterification reaction between
15 the dialkyl carbonate and the aromatic monohydroxy compound is taken as is as the starting material in the present invention without unreacted material or the catalyst being separated therefrom is also preferable. Note that, in the case of industrial implementation as in the present invention, as the dialkyl carbonate and aromatic monohydroxy compound used for obtaining the alkyl aryl carbonate that is taken as
20 the starting material in the present invention, besides fresh dialkyl carbonate and aromatic monohydroxy compound newly introduced into the reaction system, it is also preferable to use dialkyl carbonate and aromatic monohydroxy compound recovered from this process and / or another process.

FIG. 1 is a schematic view of the continuous multi-stage distillation column in
25 one embodiment according to the present invention. The continuous multi-stage distillation column according to the present invention comprises a structure having a

pair of end plates 5 above and below a cylindrical trunk portion 7 having a length L (cm) and an inside diameter D (cm) and having an internal 6 with a number of stages n thereinside, and further comprises a gas outlet 1 having an inside diameter d_1 (cm) at the top of the column or in an upper portion of the column near to the top, a liquid outlet 2 having an inside diameter d_2 (cm) at the bottom of the column or in a lower portion of the column near to the bottom, at least one inlet 3 in the upper portion and/or a middle portion of the column below the gas outlet 1, and at least one inlet 4 in the lower portion of the column above the liquid outlet 2. It should be noted that the term "in an upper portion of the column near to the top" refers to the portion extending downwardly from the top of the column to the location measuring about 0.25 L, and the term "in a lower portion of the column near to the bottom" refers to the portion extending upwardly from the bottom of the column to the location measuring about 0.25L. Note that L is defined above.

The reactive distillation column used in the present invention must have a specified structure. That is, the reactive distillation column must be made to satisfy various conditions so as to be able to carry out not only distillation but also reaction at the same time in the present process of the present invention so as to be able to produce the high boiling point reaction mixture containing the diaryl carbonate in an amount able to give not less than 1 ton / hr of a high-purity diaryl carbonate stably for a prolonged period of time. In other words, the reactive distillation column satisfies not only conditions from the perspective of the distillation function, but rather these conditions are combined with conditions required so as make the reaction proceed stably and with high selectivity. Specifically, the reactive distillation column must be a continuous multi-stage distillation column, in which L, D, n, d_1 , and d_2 satisfy the following formulae (1) to (6):

$$1500 \leq L \leq 8000 \quad (1)$$

$$100 \leq D \leq 2000 \quad (2)$$

$$2 \leq L / D \leq 40 \quad (3)$$

$$10 \leq n \leq 80 \quad (4)$$

$$2 \leq D / d_1 \leq 15 \quad (5)$$

$$5 \leq D / d_2 \leq 30 \quad (6).$$

It has been discovered that by using the continuous multi-stage distillation column that simultaneously satisfies the formulae (1), (2), (3), (4), (5) and (6), the high boiling point reaction mixture containing the diaryl carbonate can be produced from the reaction mixture containing the alkyl aryl carbonate with high selectivity and high productivity stably for a prolonged period of time, for example not less than 2000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours in an amount enabling a high-purity diaryl carbonate to be produced on an industrial scale between 1 ton / hr and 50 ton / hr. The reason why it has become possible to produce the diaryl carbonate on an industrial scale with such excellent effects by implementing the process of the present invention is not clear, but this is supposed to be due to a combined effect brought about when the conditions of formulae (1) to (6) are combined. Preferable ranges for the respective factors are described below.

If L (cm) is less than 1500, then the reaction ratio decreases and it is not possible to attain the desired production amount. Moreover, to keep down the equipment cost while securing the reaction ratio enabling the desired production amount to be attained, L must be made to be not more than 8000. A more preferable range for L (cm) is $2000 \leq L \leq 6000$, with $2500 \leq L \leq 5000$ being yet more preferable.

If D (cm) is less than 100, then it is not possible to attain the desired production amount. Moreover, to keep down the equipment cost while attaining the

desired production amount, D must be made to be not more than 2000. A more preferable range for D (cm) is $150 \leq D \leq 1000$, with $200 \leq D \leq 800$ being yet more preferable.

If L / D is less than 2 or greater than 40, then stable operation becomes
5 difficult. In particular, if L / D is greater than 40, then the pressure difference between the top and bottom of the column becomes too great, and hence prolonged stable operation becomes difficult. Moreover, it is necessary to increase the temperature in the lower portion of the column, and hence side reactions become
10 preferable range for L / D is $3 \leq L / D \leq 30$, with $5 \leq L / D \leq 15$ being yet more preferable.

If n is less than 10, then the reaction ratio decreases and it is not possible to attain the desired production amount. Moreover, to keep down the equipment cost while securing the reaction ratio enabling the desired production amount to be
15 attained, n must be made to be not more than 80. Furthermore, if n is greater than 80, then the pressure difference between the top and bottom of the column becomes too great, and hence prolonged stable operation becomes difficult. Moreover, it is necessary to increase the temperature in the lower portion of the column, and hence side reactions become liable to occur, thereby bringing about a decrease in
20 the selectivity. A more preferable range for n is $15 \leq n \leq 60$, with $20 \leq n \leq 50$ being yet more preferable.

If D / d_1 is less than 2, then the equipment cost becomes high. Moreover, since large amounts of gaseous components are readily released to the outside of the system, the stable operation becomes difficult. If D / d_1 is greater than 15, then
25 the gaseous component withdrawal amount becomes relatively low. Moreover, the stable operation becomes difficult, and a decrease in the reaction ratio is brought

about. A more preferable range for D / d_1 is $2.5 \leq D / d_1 \leq 12$, with $3 \leq D / d_1 \leq 10$ being yet more preferable.

If D / d_2 is less than 5, then the equipment cost becomes high. Moreover, the liquid withdrawal amount becomes relatively high, and hence stable operation becomes difficult. If D / d_2 is greater than 30, then the flow rate through the liquid outlet and piping become excessively fast, and erosion becomes liable to occur, thereby bringing about corrosion of the apparatus. A more preferable range for D / d_2 is $7 \leq D / d_2 \leq 25$, with $9 \leq D / d_2 \leq 20$ being yet more preferable.

Furthermore, it has been found in the present invention that it is further preferable for d_1 and d_2 to satisfy the formula (18):

$$1 \leq d_2 / d_1 \leq 6 \quad (18).$$

The term "prolonged stable operation" used in the present invention means that operation has been carried out continuously in a steady state for not less than 1000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours without clogging of piping, erosion and so on, and a prescribed amount of the diaryl carbonate has been produced while maintaining high selectivity.

The term "selectivity" for the diaryl carbonate in the reactive distillation process in the present invention is based on the alkyl aryl carbonate reacted. In the present invention, a high selectivity of not less than 95% can generally be attained, preferably not less than 97%, more preferably not less than 99%.

The continuous multi-stage distillation column used as the reactive distillation column in the present invention is preferably a distillation column having a tray and/or a packing as the internal. The term "internal" used in the present invention means the parts in the distillation column where gas and liquid are actually brought into contact with one another. As the tray, for example, a bubble-cap tray, a sieve tray, a valve tray, a counterflow tray, a Superfrac tray, a Maxfrac tray or the like are

preferable. As the packing, irregular packings such as a Raschig ring, a Lessing ring, a Pall ring, a Berl saddle, an Intalox saddle, a Dixon packing, a McMahon packing or Heli-Pak, or a structured packing such as Mellapak, Gempak, TECHNO-PAK, Flexipac, a Sulzer packing, a Goodroll packing or a Glitchgrid are preferable. The multi-stage distillation column having both a tray portion and a portion packed with the packing can also be used. Note that the term "number of stages (n) of an internal" used in the present invention means that the total number of trays in the case of a tray, and the theoretical number of stages in the case of the packing. Accordingly, in the case of the multi-stage column having both the tray portion and the portion packed with the packing, n means the sum of the total number of trays and the theoretical number of stages of the packing.

The reaction between the alkyl aryl carbonate and the aromatic monohydroxy compound present in the system in the present invention has an extremely low equilibrium constant, and moreover the reaction rate is slow.

Furthermore, the disproportionation reaction of the alkyl aryl carbonate that is the main reaction is also an equilibrium reaction, and has a low equilibrium constant, and a slow reaction rate. It has been discovered that a multi-stage distillation column having both the packing and the trays as the internals is preferable as the continuous multi-stage distillation column used in the reactive distillation for carrying out these reactions in the present invention. It is preferable for this distillation column to have a portion packed with the packing installed in the upper portion of the distillation column, and a tray portion installed in the lower portion of the distillation column. Moreover, in the present invention, the packing is preferably a structured packing, it further being preferable to use one or a plurality of sets thereof. The structured packing is preferably of at least one type selected from Mellapak, Gempak, TECHNO-PAK, Flexipac, a Sulzer packing, a Goodroll packing, and a Glitchgrid.

Furthermore, it has been discovered that, as the tray installed in the reactive distillation column according to the present invention, a sieve tray having a sieve portion and a down comer portion is particularly good in terms of the relationship between performance and equipment cost. It has also been discovered that the
5 sieve tray preferably has 100 to 1000 holes/m² in the sieve portion. A more preferable number of holes is 120 to 900 holes/m², yet more preferably 150 to 800 holes/m². Moreover, it has been discovered that the cross-sectional area per hole of the sieve tray is preferably in a range of from 0.5 to 5 cm². A more preferable cross-sectional area per hole is 0.7 to 4 cm², yet more preferably 0.9 to 3 cm².
10 Further, it has been discovered that it is particularly preferable if the sieve tray has 100 to 1000 holes/m² in the sieve portion and the cross-sectional area per hole is in a range of from 0.5 to 5 cm². Furthermore, it has been discovered that it is particularly preferable if the structured packing is of at least one type selected from Mellapak, Gempak, TECHNO-PAK, Flexipac, Sulzer packings, a Goodroll packing,
15 and a Glitchgrid, and each sieve tray has 100 to 1000 holes/m² in the sieve portion, and the cross-sectional area per hole is in a range of from 0.5 to 5 cm². It has been shown that by adding the above conditions to the reactive distillation column, the object of the present invention can be attained more easily.

When carrying out the reactive distillation process in the present invention, a
20 diaryl carbonate is produced continuously by continuously feeding the starting material containing the alkyl aryl carbonate into the continuous multi-stage distillation column in which a homogeneous catalyst is present, carrying out reaction and distillation simultaneously in the column, continuously withdrawing a low boiling point reaction mixture containing a produced dialkyl carbonate and alcohol from an upper
25 portion of the column in a gaseous form, and continuously withdrawing a high boiling point reaction mixture having the diaryl carbonate as a main product therein from a

lower portion of the column in a liquid form. In the present invention, the method of making the catalyst be present in the reactive distillation column may be any method, but because the catalyst is a homogeneous catalyst that dissolves in the starting material or the reaction liquid, it is preferable to feed the catalyst into the distillation column from a position above the middle portion of the distillation column. In this case, the catalyst liquid dissolved in the starting material or reaction liquid may be introduced into the column together with the starting material, or may be introduced into the column from a different inlet to the starting material. Moreover, a catalyst contained in the starting material containing the alkyl aryl carbonate that was used in the production of this starting material may also be preferably taken as is as the catalyst in the present reactive distillation process; in this case, fresh catalyst can also be added according to need. The amount of the catalyst used in the present invention varies depending on the type of the catalyst, the types and proportions of the starting material compounds, and reaction conditions such as the reaction temperature and the reaction pressure. The amount of the catalyst is generally in a range of from 0.0001 to 30 % by weight, preferably 0.005 to 10 % by weight, more preferably 0.001 to 1 % by weight, based on the total weight of the starting material.

The low boiling point reaction mixture continuously withdrawn from the upper portion of the reactive distillation column may contain an alkyl aryl ether and aromatic monohydroxy compound present in the system, unreacted alkyl aryl carbonate, and so on. This low boiling point reaction mixture is preferably reused by recycling to the reactor in which the transesterification reaction between the dialkyl carbonate and the aromatic monohydroxy compound is carried out. Moreover, in the present invention, a process is preferable in which a reflux operation of condensing the gaseous component withdrawn from the top of the reactive distillation column, and then returning some of this component into the upper portion of the distillation

column is carried out. In this case, the reflux ratio is in a range of from 0.05 to 10, preferably 0.08 to 5, more preferably 0.1 to 2.

In the present invention, when continuously feeding the starting material containing the alkyl aryl carbonate into the reactive distillation column, this starting material is preferably fed into the distillation column in a liquid form and/or a gaseous form from inlet(s) provided in one or a plurality of positions in the upper portion or the middle portion of the column below the gas outlet in the upper portion of the distillation column. Moreover, in the case of using a distillation column having the packing portion in the upper portion thereof and the tray portion in the lower portion thereof, which is a preferable embodiment according to the present invention, it is preferable for at least one position where an inlet is installed to be between the packing portion and the tray portion. Moreover, in the case that the packing comprises a plurality of sets of the structured packings, a method in which an inlet is installed in a space between the sets of the structured packings is preferable.

The reaction time for the transesterification reaction carried out in the present invention is considered to equate to the average residence time of the reaction liquid in the reactive distillation column. The reaction time varies depending on the form of the internal in the reactive distillation column and the number of stages, the amount of the starting material fed into the column, the type and amount of the catalyst, the reaction conditions and so on. The reaction time is generally in a range of from 0.01 to 10 hours, preferably 0.05 to 5 hours, more preferably 0.1 to 3 hours.

The reaction temperature varies depending on the type of the starting material compounds used, and the type and amount of the catalyst. The reaction temperature is generally in a range of from 100 to 350°C. It is preferable to increase the reaction temperature so as to increase the reaction rate. However, if

the reaction temperature is too high, then side reactions become liable to occur, for example production of by-products such as Fries rearrangement products of the diaryl carbonate and an alkyl aryl ether, and ester compounds thereof increases, which is undesirable. For this reason, the reaction temperature is preferably in a
5 range of from 130 to 280°C, more preferably 150 to 260°C, yet more preferably 180 to 240°C. Moreover, the reaction pressure varies depending on the type of the starting material compounds used and the composition of the starting material, the reaction temperature and so on. The reaction pressure may be any of a reduced pressure, normal pressure, or an applied pressure. The pressure at the top of the
10 column is generally in a range of from 0.1 to 2×10^7 Pa, preferably 10^3 to 10^6 Pa, more preferably 5×10^3 to 10^5 Pa.

In the present invention, the high boiling point reaction mixture containing the diaryl carbonate continuously withdrawn from the lower portion of the reactive distillation column generally contains the catalyst, the dialkyl carbonate, the aromatic
15 monohydroxy compound, the alkyl aryl carbonate, by-products and so on in addition to the diaryl carbonate. As the by-products, there are relatively low boiling point by-products such as an alkyl aryl ether, and high boiling point by-products such as Fries rearrangement products of the alkyl aryl carbonate or the diaryl carbonate and derivatives thereof, degeneration products of the diaryl carbonate, and other high
20 boiling point material of unknown structure. For example, in the case of producing diphenyl carbonate using dimethyl carbonate and phenol as starting material compounds, reaction by-products are anisole, methyl salicylate, phenyl salicylate, xanthone, phenyl methoxybenzoate,
1-phenoxy carbonyl-2-phenoxy carboxy-phenylene and so on, and typically a small
25 amount of the high boiling point by-products of unknown structure thought to be produced through further reaction of these reaction by-products is also contained.

In the present invention, the high boiling point reaction mixture containing the diaryl carbonate continuously withdrawn from the lower portion of the reactive distillation column is continuously introduced into a high boiling point material separating column A, and continuously separated into a column top component A_T containing the diaryl carbonate and a column bottom component A_B containing the catalyst, and then the column top component A_T is continuously introduced into a diaryl carbonate purifying column B having a side cut outlet, and continuously separated by distillation into a column top component B_T , a side cut component B_S and a column bottom component B_B . Not less than 1 ton / hr of a high-purity diaryl carbonate is obtained continuously as the side cut component B_S . For this purpose, the high boiling point material separating column A and the diaryl carbonate purifying column B must each be made to be a continuous multi-stage distillation column having a specified structure, and must be used in combination with one another.

Figure 2 illustrates a schematic view of an example showing a continuous separating / purifying apparatus for carrying out the present invention in which a high boiling point material separating column A and a diaryl carbonate purifying column B are connected together. As one example, each of the high boiling point material separating column A and the diaryl carbonate purifying column B comprises continuous multi-stage distillation columns having therein an internal comprising, but is not limited to, a structured packing having a predetermined number of stages. Note that the columns A and B comprise the following structures, respectively, in order to carry out the producing process according to the present invention.

The high boiling point material separating column A used in the present invention must be a continuous multi-stage distillation column having a length L_A (cm), an inside diameter D_A (cm), and an internal with a number of stages n_A therein, wherein L_A , D_A , and n_A satisfy the following formulae (7) to (9):

$$800 \leq L_A \leq 3000 \quad (7)$$

$$100 \leq D_A \leq 1000 \quad (8)$$

$$20 \leq n_A \leq 100 \quad (9).$$

Moreover, the distillation conditions for the high boiling point material

5 separating column A are preferably a column bottom temperature T_A in a range of from 185 to 280°C, and a column top pressure P_A in a range of from 1000 to 20000 Pa.

Furthermore, the diaryl carbonate purifying column B must be a continuous multi-stage distillation column having a length L_B (cm), an inside diameter D_B (cm),
 10 an internal therein, an inlet B1 at an intermediate portion of the column, and a side cut outlet B2 between the inlet B1 and the column bottom, in which a number of stages of the internals above the inlet B1 is n_1 , a number of stages of the internal between the inlet B1 and the side cut outlet B2 is n_2 , a number of stages n_3 of the internals below the side cut outlet B2 is n_3 , and a total number of stages is $n_B (= n_1 +$
 15 $n_2 + n_3)$, wherein L_B , D_B , n_1 , n_2 , n_3 , and n_B satisfy the following formulae (10) to (15):

$$1000 \leq L_B \leq 5000 \quad (10)$$

$$100 \leq D_B \leq 1000 \quad (11)$$

$$5 \leq n_1 \leq 20 \quad (12)$$

$$12 \leq n_2 \leq 40 \quad (13)$$

$$20 \quad 3 \leq n_3 \leq 15 \quad (14)$$

$$20 \leq n_B \leq 70 \quad (15).$$

Moreover, the distillation conditions for the diaryl carbonate purifying column B are preferably a column bottom temperature T_B in a range of from 185 to 280°C, and a column top pressure P_B in a range of from 1000 to 20000 Pa.

25 It has been discovered that by using the high boiling point material separating column A and the diaryl carbonate purifying column B simultaneously

satisfying all of these conditions, a high-purity diaryl carbonate can be produced on an industrial scale between 1 ton / hr and 50 ton / hr stably for a prolonged period of time, for example not less than 2000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours, from the high boiling point reaction mixture containing the diaryl carbonate. The reason why it has become possible to produce a high-purity diaryl carbonate on an industrial scale with such excellent effects by implementing the process of the present invention is not clear, but this is supposed to be due to a combined effect between the distillation conditions and an effect brought about when the conditions of formulae (7) to (15) are combined. Preferable ranges for the respective factors are described below.

If L_A (cm) is less than 800, since a height of the internal which can be installed in the high boiling point material separating column A becomes limited, the separation efficiency decreases, and it is thus undesirable for L_A (cm). Moreover, to keep down the equipment cost while attaining the desired separation efficiency, L_A must be made to be not more than 3000. A more preferable range for L_A (cm) is $1000 \leq L_A \leq 2500$, with $1200 \leq L_A \leq 2000$ being yet more preferable.

If D_A (cm) is less than 100, then it is not possible to attain the desired production amount. Moreover, to keep down the equipment cost while attaining the desired production amount, D_A must be made to be not more than 1000. A more preferable range for D_A (cm) is $200 \leq D_A \leq 600$, with $250 \leq D_A \leq 450$ being yet more preferable.

If n_A is less than 20, then the separation efficiency decreases, and hence the desired high purity cannot be attained. Moreover, to keep down the equipment cost while attaining the desired separation efficiency, n_A must be made to be not more than 100. Furthermore, if n_A is greater than 100, then the pressure difference between the top and bottom of the column becomes too great, and hence prolonged

stable operation of the high boiling point material separating column A becomes difficult. Moreover, it becomes necessary to increase the temperature in the lower portion of the column, and hence side reactions become liable to occur, which is undesirable. A more preferable range for n_A is $30 \leq n_A \leq 70$, with $35 \leq n_A \leq$
 5 60 being yet more preferable.

If T_A is less than 185°C , since the column top pressure must be reduced, equipment for maintaining a high vacuum must be used, and moreover the equipment increases in size. Moreover, it is undesirable for T_A to be greater than 280°C , because the high boiling point by-products are produced during the distillation.
 10 A more preferable range for T_A is from 190 to 240°C , with from 195 to 230°C being yet more preferable.

It is undesirable for P_A to be less than 1000 Pa, since then large equipment enabling a high vacuum to be maintained must be used. Moreover, it is undesirable for P_A to be greater than 20000 Pa, since then the distillation temperature must be
 15 increased and hence production of by-products increases. A more preferable range for P_A is from 2000 to 15000 Pa, with from 3000 to 13000 Pa being yet more preferable.

If L_B (cm) is less than 1000 , since a height of the internal which can be installed in the diaryl carbonate purifying column B becomes limited, the separation
 20 efficiency decreases, and it is thus undesirable for L_B (cm). Moreover, to keep down the equipment cost while attaining the desired separation efficiency, L_B must be made to be not more than 5000 . A more preferable range for L_B (cm) is $1500 \leq L_B \leq 3000$, with $1700 \leq L_B \leq 2500$ being yet more preferable.

If D_B (cm) is less than 100 , then it is not possible to attain the desired
 25 production amount. Moreover, to keep down the equipment cost while attaining the desired production amount, D_B must be made to be not more than 1000 . A more

preferable range for D_B (cm) is $150 \leq D_B \leq 500$, with $200 \leq D_B \leq 400$ being yet more preferable.

If n_B is less than 20, then the separation efficiency for the column as a whole decreases, and hence the desired high purity cannot be attained. Moreover, to
 5 keep down the equipment cost while attaining the desired separation efficiency, n_B must be made to be not more than 70. Furthermore, if n_B is greater than 70, then the pressure difference between the top and bottom of the column becomes too great, and hence prolonged stable operation of the diaryl carbonate purifying column B becomes difficult. Moreover, it becomes necessary to increase the temperature in
 10 the lower portion of the column, and hence side reactions become liable to occur, which is undesirable. A more preferable range for n_B is $25 \leq n_B \leq 55$, with $30 \leq n_B \leq 50$ being yet more preferable. Furthermore, it has been ascertained that to obtain the desired high-purity diphenyl carbonate stably for a prolonged period of time, n_1 , n_2 , and n_3 must be in the ranges $5 \leq n_1 \leq 20$, $12 \leq n_2 \leq 40$, and $3 \leq$
 15 $n_3 \leq 15$, respectively. More preferable ranges are $7 \leq n_1 \leq 15$, $12 \leq n_2 \leq 30$, and $3 \leq n_3 \leq 10$.

It is undesirable for T_B to be less than 185°C, since then the column top pressure must be reduced, and hence equipment for maintaining a high vacuum must be used, and moreover the equipment increases in size. Moreover, it is
 20 undesirable for T_B to be greater than 280°C, since then high boiling point by-products are produced during the distillation. A more preferable range for T_B is from 190 to 240°C, with from 195 to 230°C being yet more preferable.

It is undesirable for P_B to be less than 1000 Pa, since then large equipment enabling a high vacuum to be maintained must be used. Moreover, it is undesirable
 25 for P_B to be greater than 20000 Pa, since then the distillation temperature must be increased and hence production of by-products increases. A more preferable range

for P_B is from 2000 to 15000 Pa, with from 3000 to 13000 Pa being yet more preferable.

For the high boiling point material separating column A and the diaryl carbonate purifying column B, so long as D_A and D_B are within the above ranges, each of the columns may have the same inside diameter from the upper portion thereof to the lower portion thereof, or the inside diameter may differ in different portions. For example, for each of the continuous multi-stage distillation columns, the inside diameter of the upper portion of the column may be smaller than, or larger than, the inside diameter of the lower portion of the column.

Each of the high boiling point material separating column A and the diaryl carbonate purifying column B used in the present invention is a distillation column having a tray and/or a packing as the internal. The term "internal" used in the present invention means the parts in the distillation column where gas and liquid are actually brought into contact with one another. The multi-stage distillation column having both a tray portion and a portion packed with the packing can also be used. Note that the term "number of stages (n) of an internal" used in the present invention means that the total number of trays in the case of a tray, and the theoretical number of stages in the case of the packing. Accordingly, in the case of the multi-stage column having both the tray portion and the portion packed with the packing, n means the sum of the total number of trays and the theoretical number of stages of the packing.

It has been ascertained that in the present invention, the high boiling point material separating column A preferably has the packing as the internal, and furthermore a structured packing is preferable as the packing. Moreover, it has been discovered that the diaryl carbonate purifying column B preferably has the packing as the internal, particularly preferably one set or a plurality of sets of the

structured packing.

In the present invention, the column bottom liquid continuously withdrawn from the bottom of the reactive distillation column is preferably fed into the high boiling point material separating column A as is. This high boiling point reaction mixture continuously withdrawn from the bottom of the reactive distillation column generally contains 0.05 to 2 % by weight of the dialkyl carbonate, 1 to 20 % by weight of the aromatic monohydroxy compound, 0.05 to 2 % by weight of an alkyl aryl ether, 10 to 45 % by weight of the alkyl aryl carbonate, 50 to 80 % by weight of the diaryl carbonate, 0.1 to 5 % by weight of high boiling point by-products, and 0.001 to 5 % by weight of the catalyst. The composition of the high boiling point reaction mixture varies depending on the reactive distillation conditions, the type and amount of the catalyst and so on, but so long as the reactive distillation is carried out under constant conditions, a high boiling point reaction mixture of approximately constant composition can be produced, and hence the composition of the high boiling point reaction mixture fed into the high boiling point material separating column A may be approximately constant. However, in the present invention, so long as the composition of the high boiling point reaction mixture is within the above range, then even if this composition fluctuates somewhat, the separation can still be carried out with approximately the same separation efficiency. This is one of the characteristic features of the present invention.

In the present invention, when continuously feeding the high boiling point reaction mixture into the high boiling point material separating column A, the high boiling point reaction mixture may be fed in as a liquid from inlet(s) provided in one or a plurality of positions below a middle portion of the separating column A, or it is also preferable to feed the high boiling point reaction mixture into the column via a reboiler of the separating column A from piping provided at a lower portion of the

reboiler. The amount of the high boiling point reaction mixture fed into the high boiling point material separating column A varies according to the amount of the high-purity diaryl carbonate to be produced, the concentration of the diaryl carbonate in the high boiling point reaction mixture, the separation conditions for the separating column A and so on. The high boiling point reaction mixture used in the present invention generally contains 50 to 80 % by weight of the diaryl carbonate, and hence to obtain between 1 ton / hr and 50 ton / hr of the high-purity diaryl carbonate, although dependent on the diaryl carbonate content, the amount of the high boiling point reaction mixture continuously introduced into the high boiling point material separating column A is not less than approximately 1.3 to 2 ton / hr but not more than 100 ton / hr. This amount is generally not less than approximately 2 ton / hr, preferably not less than approximately 6 ton / hr, more preferably not less than approximately 10 ton / hr. The upper limit of this amount varies according to the size of the apparatus, the required production amount and so on, but is generally 200 ton / hr.

The high boiling point reaction mixture fed continuously into the high boiling point material separating column A is separated into a column top component (A_T) comprising most of the diaryl carbonate and most of compounds having a lower boiling point than that of the diaryl carbonate such as unreacted starting material, an alkyl aryl ether and the alkyl aryl carbonate, and a column bottom component (A_B) containing the catalyst, by-products having a higher boiling point than that of the diaryl carbonate and a small amount of the diaryl carbonate. The column bottom component (A_B) may contain a small amount of the alkyl aryl carbonate. Such organic material in the column bottom component plays a useful role in dissolving the catalyst component and thus maintaining a liquid state. It is generally preferable for all or some of the column bottom component (A_B) to be reused by recycling to the

reactor in which the transesterification reaction between the dialkyl carbonate and the aromatic monohydroxy compound is carried out and/or the reactive distillation column as a transesterification reaction catalyst component.

In the present invention, in the case, for example, of using unsubstituted phenol or a lower hydrocarbon-substituted phenol as the aromatic monohydroxy compound, the catalyst component and by-products having a higher boiling point than that of diphenyl carbonate such as phenyl salicylate, xanthone, phenyl methoxybenzoate and 1-phenoxycarbonyl-2-phenoxycarboxy-phenylene or by-products having a higher boiling point than that of the lower hydrocarbon-substituted diphenyl carbonate such as lower hydrocarbon-substituted derivatives of the above compounds are almost completely removed as the column bottom component (A_B) in the high boiling point material separating column A.

It is a characteristic feature of the present invention that it is easy to make the content of the catalyst component and the by-products having a higher boiling point than that of the diaryl carbonate in the column top component (A_T) be generally not more than 200 ppm, preferably not more than 100 ppm, more preferably not more than 50 ppm. It is another characteristic feature of the present invention that despite making the column top component (A_T) hardly contain any such high boiling point by-products, most of the diaryl carbonate in the reaction mixture introduced can be withdrawn from the top of the column. In the present invention, not less than 95%, preferably not less than 96%, more preferably not less than 98%, of the diaryl carbonate in the reaction mixture continuously fed into the high boiling point material separating column A can be withdrawn from the top of the column.

Moreover, in the present invention, although dependent on the composition of the reaction mixture fed into the separating column A, typically 90 to 97 % by weight of the liquid continuously fed in is continuously withdrawn from the top of the

column as the column top component (A_T), with 10 to 3 % by weight being continuously withdrawn from the bottom of the column as the column bottom component (A_B). The composition of the column top component (A_T) is generally 0.05 to 2 % by weight of the dialkyl carbonate, 1 to 21 % by weight of the aromatic monohydroxy compound, 0.05 to 2 % by weight of an alkyl aryl ether, 11 to 47 % by weight of the alkyl aryl carbonate, and 52 to 84 % by weight of the diaryl carbonate, based on 100 % by weight of the column top component. The content of high boiling point by-products is generally not more than 200 ppm, preferably not more than 100 ppm, more preferably not more than 50 ppm.

In the present invention, the reflux ratio for the high boiling point material separating column A is in a range of from 0.01 to 10, preferably from 0.08 to 5, more preferably from 0.1 to 3.

As stated above, the amount of the column top component (A_T) continuously withdrawn from the top of the high boiling point material separating column A is generally approximately 90 to 97% of the reaction mixture fed into the separating column A. This column top component (A_T) is continuously fed as is into the diaryl carbonate purifying column B from the inlet B1 provided at an intermediate portion of the purifying column B, and is continuously separated into three components, i.e. a column top component (B_T), a side cut component (B_S), and a column bottom component (B_B). All of components having a lower boiling point than that of the diaryl carbonate contained in the column top component (A_T) from the separating column A fed into the purifying column B are continuously withdrawn from the top of the purifying column B as the column top component (B_T), and a small amount of liquid is continuously withdrawn from the bottom of the purifying column B. A small amount of the diaryl carbonate is contained in the column top component (B_T), this amount generally being 1 to 9%, preferably 3 to 8%, of the diaryl carbonate fed in.

The diaryl carbonate in the column top component (B_T) is separated out and thus recovered in another distillation column used for separating the column top component (B_T). Alternatively, a method in which this diaryl carbonate is separated off as the column bottom component from this other distillation column, and is then
5 recovered by being returned into the high boiling point material separating column A and/or the diaryl carbonate purifying column B is also preferable.

The column bottom component (B_B) contains the diaryl carbonate, and a small amount of high boiling point by-products concentrated to approximately a few percent. Another characteristic feature of the present invention is that the amount
10 of the diaryl carbonate in the column bottom component (B_B) withdrawn from the bottom of the purifying column B can be kept very low. This amount is generally 0.05 to 0.5% of the diaryl carbonate fed in.

The high-purity diaryl carbonate is continuously withdrawn from the side cut outlet B2 at a flow rate of generally not less than 1 ton / hr, preferably not less than 3
15 ton / hr, more preferably not less than 5 ton / hr, and not more than 50 ton / hr. This amount generally corresponds to approximately 90 to 96% of the diaryl carbonate fed into the purifying column B.

The purity of the diaryl carbonate obtained as the side cut component (B_S) in the present invention is generally not less than 99.9%, preferably not less than
20 99.99%, more preferably not less than 99.999%. The contents of high boiling point impurities when carrying out the present invention using an alkyl aryl carbonate obtained through a transesterification reaction between a dialkyl carbonate and phenol or a lower hydrocarbon-substituted phenol are not more than 30 ppm, preferably not more than 10 ppm, more preferably not more than 1 ppm for phenyl
25 salicylate or a lower hydrocarbon-substituted derivative thereof, not more than 30 ppm, preferably not more than 10 ppm, more preferably not more than 1 ppm for

xanthone, not more than 30 ppm, preferably not more than 10 ppm, more preferably not more than 1 ppm for phenyl methoxybenzoate or a lower hydrocarbon-substituted derivative thereof, and not more than 30 ppm, preferably not more than 10 ppm, more preferably not more than 5 ppm for

5 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene or a lower hydrocarbon-substituted derivative thereof. Moreover, the total content of these high boiling point by-products is not more than 100 ppm, preferably not more than 50 ppm, more preferably not more than 10 ppm. Note that the term "high-purity diaryl carbonate" used in the present invention means that the purity of the diaryl carbonate is not less
10 than 99.9 and the diaryl carbonate contains not more than 100 ppm of high boiling point by-products.

Moreover, in the present invention, a starting material and catalyst not containing a halogen are generally used, and hence the halogen content of the diaryl carbonate obtained is not more than 0.1 ppm, preferably not more than 10 ppb, more
15 preferably not more than 1 ppb.

In the present invention, the reflux ratio for the diaryl carbonate purifying column B is in a range of from 0.01 to 10, preferably from 0.1 to 8, more preferably from 0.5 to 5.

The material constituting the reactive distillation column, the high boiling
20 point material separating column A, the diaryl carbonate purifying column B, and other liquid-contacting parts in the present invention is generally a metallic material such as carbon steel or stainless steel. In terms of the quality of the diaryl carbonate produced, stainless steel is preferable.

25 Examples

Hereinbelow, the present invention will be described in more detail with

reference to the following Examples, but the present invention is not limited to the following Examples.

The purity of the diphenyl carbonate, and the contents of impurities were measured by means of a gas chromatography method, and the halogen content was measured by means of an ion chromatography method.

Example 1:

<Reactive distillation column>

A continuous multi-stage distillation column as shown in FIG. 1 having $L = 3100$ cm, $D = 500$ cm, $L / D = 6.2$, $n = 30$, $D / d_1 = 3.85$, and $D / d_2 = 11.1$ was used. In this example, as the internal, two sets of Mellapak (total number of stages being 11) were installed in the upper portion, the sieve tray having the cross-sectional area per hole being approximately 1.3 cm^2 and the number of holes being approximately $250/\text{m}^2$ was used as the internal.

<High boiling point material separating column A>

A continuous multi-stage distillation column as shown in FIG. 2 having $L_A = 1700$ cm and $D_A = 340$ cm, and having Mellapak with $n_A = 30$ installed therein as the internal was used as the separating column A.

<Diaryl carbonate purifying column B>

A continuous multi-stage distillation column as shown in FIG. 2 having $L_B = 2200$ cm and $D_B = 280$ cm, and having three sets of Mellapak with $n_1 = 12$, $n_2 = 18$, and $n_3 = 5$ installed therein as the internal was used as the purifying column B.

<Reactive distillation>

A reaction mixture containing 18 % by weight of methyl phenyl carbonate that had been obtained by subjecting a mixture containing dimethyl carbonate and phenol in a weight ratio of dimethyl carbonate / phenol = 1.3 to a transesterification reaction

was used as a starting material. This starting material contained 26 % by weight of dimethyl carbonate, 6 % by weight of anisole, 48 % by weight of phenol, and 1 % by weight of diphenyl carbonate, and further contained approximately 100 ppm of Pb(OPh)_2 as a catalyst. The starting material substantially did not contain halogens (outside the detection limit for the ion chromatography, i.e. 1 ppb or less).

The starting material was introduced into the reactive distillation column of FIG. 1 at a flow rate of 66 ton / hr from a starting material inlet installed between the Mellapak and the sieve trays. Reactive distillation was carried out continuously under conditions of a temperature at the bottom of the column being 210°C , a pressure at the top of the column being 3×10^4 Pa, and a reflux ratio of 0.3. It was possible to attain stable steady state operation after 24 hours. The composition of the high boiling point reaction mixture, which was continuously withdrawn at 13.1 ton / hr from the bottom of the column, was 0.1 % by weight of dimethyl carbonate, 0.1 % by weight of anisole, 6.3 % by weight of phenol, 32.2 % by weight of methyl phenyl carbonate, 58.6 % by weight of diphenyl carbonate, and 2.7 % by weight of high boiling point by-products including the catalyst.

<Separation / purification>

Using an apparatus comprising the high boiling point material separating column A and the diaryl carbonate purifying column B as shown in FIG. 2, the reaction mixture obtained through the reactive distillation described above was continuously introduced at 13.1 ton / hr into the separating column A from the inlet A1. The column bottom temperature (T_A) was made to be 206°C and the column top pressure (P_A) was made to be 3800 Pa in the separating column A, distillation was carried out continuously with a reflux ratio of 0.6, a column top component (A_T) was continuously withdrawn at 12.5 ton / hr via a conduit 16, and a column bottom component (A_B) was continuously withdrawn at 0.6 ton / hr via a conduit 11. The

column top component (A_T) was continuously introduced as is into the purifying column B from the inlet B1. The column bottom temperature (T_B) was made to be 213°C and the column top pressure (P_B) was made to be 5000 Pa in the purifying column B, distillation was carried out continuously with a reflux ratio of 1.5, a column
5 top component (B_T) was continuously withdrawn at 5.3 ton / hr via a conduit 26, a column bottom component (B_B) was continuously withdrawn at 0.03 ton / hr via a conduit 31, and a side cut component (B_S) was continuously withdrawn at 7.17 ton / hr via a conduit 33.

The compositions of the components at 24 hours after the system had

10 become completely stable were as follows:

A_T : 0.1 % by weight of dimethyl carbonate, 0.1 % by weight of anisole, 6.6 % by weight of phenol, 33.8 % by weight of methyl phenyl carbonate, 59.4 % by weight of diphenyl carbonate;

A_B : 41.0 % by weight of diphenyl carbonate, 59.0 % by weight of high boiling point
15 material including a catalyst component and by-products having a higher boiling point than that of diphenyl carbonate such as phenyl salicylate, xanthone, phenyl methoxybenzoate and 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene;

B_T : 0.25 % by weight of dimethyl carbonate, 0.25 % by weight of anisole, 15.6 % by weight of phenol, 79.6 % by weight of methyl phenyl carbonate, 4.3 % by weight of
20 diphenyl carbonate;

B_B : 95.0 % by weight of diphenyl carbonate, 5.0 % by weight of high boiling point material.

The content of each of phenyl salicylate, xanthone and phenyl methoxybenzoate in the side cut component was not more than 1 ppm, and the
25 content of 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene was 4 ppm. Moreover, the halogen content was not more than 1 ppb. It was thus found that the purity of

the diphenyl carbonate obtained from the side cut was not less than 99.999%.

Moreover, the amount of this high-purity diphenyl carbonate produced was 7.17 ton / hr.

Prolonged continuous operation was carried out under these conditions.

- 5 The amount of diphenyl carbonate produced and the purity were substantially unchanged after 500 hours, 2000 hours, 4000 hours, 5000 hours, and 6000 hours.

Example 2:

<Reactive distillation>

- 10 A mixture containing 21 % by weight of methyl phenyl carbonate that had been obtained by subjecting a mixture containing dimethyl carbonate and phenol in a weight ratio of dimethyl carbonate / phenol = 1.9 to a transesterification reaction was used as a starting material. This starting material contained 32 % by weight of dimethyl carbonate, 5 % by weight of anisole, 41 % by weight of phenol, and 1 % by
15 weight of diphenyl carbonate, and further contained approximately 250 ppm of Pb(OPh)_2 as a catalyst. The starting material substantially did not contain halogens (outside the detection limit for the ion chromatography, i.e. 1 ppb or less).

- The starting material was introduced into the reactive distillation column of FIG. 1 at a flow rate of 80 ton / hr from a starting material inlet installed between the
20 Mellapak and the sieve trays. Reactive distillation was carried out continuously under conditions of a temperature at the bottom of the column being 205°C, a pressure at the top of the column being 2×10^4 Pa, and a reflux ratio of 0.5. It was possible to attain stable steady state operation after 24 hours. The composition of the high boiling point reaction mixture, which was continuously withdrawn at 11.3 ton
25 / hr from the bottom of the column, was 0.1 % by weight of dimethyl carbonate, 0.1 % by weight of anisole, 2.5 % by weight of phenol, 33.2 % by weight of methyl phenyl

carbonate, 62.5 % by weight of diphenyl carbonate, and 1.6 % by weight of high boiling point by-products including the catalyst.

<Separation / purification>

Using an apparatus comprising the high boiling point material separating column A and the diaryl carbonate purifying column B as in Example 1, the reaction mixture obtained through the reactive distillation described above was continuously introduced at 11.3 ton / hr into the separating column A from the inlet A1. The column bottom temperature (T_A) was made to be 205°C and the column top pressure (P_A) was made to be 4000 Pa in the separating column A, distillation was carried out continuously with a reflux ratio of 0.7, a column top component (A_T) was continuously withdrawn at 11.0 ton / hr via the conduit 16, and a column bottom component (A_B) was continuously withdrawn at 0.3 ton / hr via the conduit 11. The column top component (A_T) was continuously introduced as is into the purifying column B from the inlet B1. The column bottom temperature (T_B) was made to be 210°C and the column top pressure (P_B) was made to be 4500 Pa in the purifying column B, distillation was carried out continuously with a reflux ratio of 2.0, a column top component (B_T) was continuously withdrawn at 4.7 ton / hr via the conduit 26, a column bottom component (B_B) was continuously withdrawn at 0.03 ton / hr via the conduit 31, and a side cut component (B_S) was continuously withdrawn at 6.27 ton / hr via the conduit 33.

The compositions of the components at 24 hours after the system had become completely stable were as follows:

A_T : 0.1 % by weight of dimethyl carbonate, 0.1% by weight of anisole, 2.6 % by weight of phenol, 34.1 % by weight of methyl phenyl carbonate, 63.1 % by weight of diphenyl carbonate;

A_B : 40.2 % by weight of diphenyl carbonate, 59.8 % by weight of high boiling point

material including a catalyst component and by-products having a higher boiling point than that of diphenyl carbonate such as phenyl salicylate, xanthone, phenyl methoxybenzoate and 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene;

5 B_T: 0.3 % by weight of dimethyl carbonate, 0.2 % by weight of anisole, 6.1 % by weight of phenol, 79.8 % by weight of methyl phenyl carbonate, 13.6 % by weight of diphenyl carbonate;

B_B: 96.0 % by weight of diphenyl carbonate, 4.0 % by weight of high boiling point material.

10 The content of each of phenyl salicylate, xanthone and phenyl methoxybenzoate in the side cut component was not more than 1 ppm, and the content of 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene was 3 ppm. Moreover, the halogen content was not more than 1 ppb. It was thus found that the purity of the diphenyl carbonate obtained from the side cut was not less than 99.999%. Moreover, the amount of this high-purity diphenyl carbonate produced was 6.27 ton /
15 hr.

Prolonged continuous operation was carried out under these conditions. The amount of diphenyl carbonate produced and the purity were substantially unchanged after 500 hours, 1000 hours, and 2000 hours.

20 Example 3:

<Reactive distillation>

A mixture containing 16 % by weight of methyl phenyl carbonate that had been obtained by subjecting a mixture containing dimethyl carbonate and phenol in a weight ratio of dimethyl carbonate / phenol = 1.4 to a transesterification reaction was
25 used as a starting material. This starting material contained 27 % by weight of dimethyl carbonate, 7 % by weight of anisole, 49 % by weight of phenol, and 0.5 %

by weight of diphenyl carbonate, and further contained approximately 200 ppm of Pb(OPh)_2 as a catalyst. The starting material substantially did not contain halogens (outside the detection limit for the ion chromatography, i.e. 1 ppb or less).

The starting material was introduced into the continuous multi-stage distillation column at a flow rate of 94 ton / hr from a starting material inlet installed between the Mellapak and the sieve trays. Reactive distillation was carried out continuously under conditions of a temperature at the bottom of the column being 215°C , a pressure at the top of the column being 2.5×10^4 Pa, and a reflux ratio of 0.4. It was possible to attain stable steady state operation after 24 hours. The composition of the high boiling point reaction mixture, which was continuously withdrawn at 17.2 ton / hr from the bottom of the column, was 0.2 % by weight of dimethyl carbonate, 0.1 % by weight of anisole, 6.6 % by weight of phenol, 30.2 % by weight of methyl phenyl carbonate, 60.1 % by weight of diphenyl carbonate, and 2.8 % by weight of high boiling point by-products including the catalyst.

15 <Separation / purification>

Using an apparatus comprising the high boiling point material separating column A and the diaryl carbonate purifying column B as in Example 1, the reaction mixture obtained through the reactive distillation described above was continuously introduced at 17.2 ton / hr into the separating column A from the inlet A1. The column bottom temperature (T_A) was made to be 207°C and the column top pressure (P_A) was made to be 4100 Pa in the separating column A, distillation was carried out continuously with a reflux ratio of 0.61, a column top component (A_T) was continuously withdrawn at 16.4 ton / hr via the conduit 16, and a column bottom component (A_B) was continuously withdrawn at 0.8 ton / hr via the conduit 11. The column top component (A_T) was continuously introduced as is into the purifying column B from the inlet B1. The column bottom temperature (T_B) was made to be

220°C and the column top pressure (P_B) was made to be 6600 Pa in the purifying column B, distillation was carried out continuously with a reflux ratio of 1.49, a column top component (B_T) was continuously withdrawn at 7.1 ton / hr via the conduit 26, a column bottom component (B_B) was continuously withdrawn at 0.05 ton / hr via the conduit 31, and a side cut component (B_S) was continuously withdrawn at 9.25 ton / hr via the conduit 33.

The compositions of the components at 24 hours after the system had become completely stable were as follows:

A_T : 0.2 % by weight of dimethyl carbonate, 0.1 % by weight of anisole, 6.9 % by weight of phenol, 31.7 % by weight of methyl phenyl carbonate, 61.1 % by weight of diphenyl carbonate;

A_B : 39.8 % by weight of diphenyl carbonate, 61.2 % by weight of high boiling point material including a catalyst component and by-products having a higher boiling point than that of diphenyl carbonate such as phenyl salicylate, xanthone, phenyl methoxybenzoate and 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene;

B_T : 0.5 % by weight of dimethyl carbonate, 0.2 % by weight of anisole, 16.0 % by weight of phenol, 73.2 % by weight of methyl phenyl carbonate, 10.1 % by weight of diphenyl carbonate;

B_B : 94.0 % by weight of diphenyl carbonate, 6.0 % by weight of high boiling point material.

The content of each of phenyl salicylate, xanthone and phenyl methoxybenzoate in the side cut component was not more than 1 ppm, and the content of 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene was 4 ppm. Moreover, the halogen content was not more than 1 ppb. It was thus found that the purity of the diphenyl carbonate obtained from the side cut was not less than 99.999%.

Moreover, the amount of this high-purity diphenyl carbonate produced was 9.25 ton /

hr.

Prolonged continuous operation was carried out under these conditions.

The amount of diphenyl carbonate produced and the purity were substantially unchanged after 500 hours, 1000 hours, and 2000 hours.

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Industrial Applicability

The present invention can be suitably used as a specific process that enables a high-purity diaryl carbonate that can be used as a raw material of a high-quality and high-performance polycarbonate to be produced stably for a
10 prolonged period of time on an industrial scale of not less than 1 ton / hr using as a starting material a reaction mixture containing an alkyl aryl carbonate obtained through a transesterification reaction between a dialkyl carbonate and an aromatic monohydroxy compound.

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CLAIMS

We claim:

1. In an industrial process for the production of a high-purity diaryl carbonate in which the high-purity diaryl carbonate is produced by taking as a starting material a reaction mixture containing an alkyl aryl carbonate, which has been obtained through a transesterification reaction between a dialkyl carbonate and an aromatic monohydroxy compound, continuously feeding the starting material into a reactive distillation column comprising a continuous multi-stage distillation column in which a homogeneous catalyst is present, carrying out a transesterification reaction and distillation simultaneously in the column, continuously withdrawing a low boiling point reaction mixture containing a produced dialkyl carbonate from an upper portion of the column in a gaseous form, and continuously withdrawing a high boiling point reaction mixture containing a diaryl carbonate from a lower portion of the column in a liquid form, continuously introducing said high boiling point reaction mixture into a high boiling point material separating column A, and continuously carrying out separation by distillation into a column top component A_T containing the diaryl carbonate and a column bottom component A_B containing the catalyst, and then continuously introducing the column top component A_T into a diaryl carbonate purifying column B having a side cut outlet, and continuously carrying out separation by distillation into a column top component B_T , a side cut component B_S and a column bottom component B_B , the improvement which comprises:

- (a) said reactive distillation column comprises a continuous multi-stage distillation column having a length L (cm), an inside diameter D (cm), an internal with a number of stages n thereinside, a gas outlet having an inside diameter d_1 (cm) at the top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_2 (cm) at the bottom of the column or in a lower

portion of the column near to the bottom, at least one inlet provided in the upper portion and/or a middle portion of the column below the gas outlet, and at least one inlet provided in the lower portion of the column above the liquid outlet, wherein L , D , n , d_1 , and d_2 satisfy the following formulae (1) to (6);

$$1500 \leq L \leq 8000 \quad (1)$$

$$100 \leq D \leq 2000 \quad (2)$$

$$2 \leq L/D \leq 40 \quad (3)$$

$$10 \leq n \leq 80 \quad (4)$$

$$2 \leq D/d_1 \leq 15 \quad (5)$$

$$5 \leq D/d_2 \leq 30 \quad (6);$$

(b) said high boiling point material separating column A comprises a continuous multi-stage distillation column having a length L_A (cm), an inside diameter D_A (cm), and an internal with a number of stages n_A thereinside, wherein L_A , D_A , and n_A satisfy the following formulae (7) to (9);

$$800 \leq L_A \leq 3000 \quad (7)$$

$$100 \leq D_A \leq 1000 \quad (8)$$

$$20 \leq n_A \leq 100 \quad (9);$$

(c) said diaryl carbonate purifying column B comprises a continuous multi-stage distillation column having a length L_B (cm), an inside diameter D_B (cm), an internal thereinside, an inlet B1 at an intermediate portion of the column, and a side cut outlet B2 between the inlet B1 and the column bottom, in which a number of stages of the internal above the inlet B1 is n_1 , a number of stages of the internals between the inlet B1 and the side cut outlet B2 is n_2 , a number of stages of the internals below the side cut outlet B2 is n_3 , and a total number of stages is $n_B (= n_1 + n_2 + n_3)$, wherein L_B , D_B , n_1 , n_2 , n_3 , and n_B satisfy the following formulae (10) to (15);

$$1000 \leq L_B \leq 5000 \quad (10)$$

$$100 \leq D_B \leq 1000 \quad (11)$$

$$5 \leq n_1 \leq 20 \quad (12)$$

$$12 \leq n_2 \leq 40 \quad (13)$$

$$3 \leq n_3 \leq 15 \quad (14)$$

$$20 \leq n_B \leq 70 \quad (15); \text{ and}$$

(d) not less than 1 ton / hr of the high-purity diaryl carbonate is obtained continuously as the side cut component B_S.

2. The process according to claim 1, wherein a distillation operation of said high boiling point material separating column A is carried out at a column bottom temperature T_A in a range of from 185 to 280°C, and at a column top pressure P_A in a range of from 1000 to 20000 Pa, and a distillation operation of said diaryl carbonate purifying column B is carried out at a column bottom temperature T_B in a range of from 185 to 280°C, and at a column top pressure P_B in a range of from 1000 to 20000 Pa.

3. The process according to claim 1 or 2, wherein L, D, L / D, and n for said reactive distillation column satisfy the following formulae; $2000 \leq L \leq 6000$, $150 \leq D \leq 1000$, $3 \leq L / D \leq 30$, and $15 \leq n \leq 60$, respectively,

L_A, D_A, and n_A for said high boiling point material separating column A satisfy the following formulae; $1000 \leq L_A \leq 2500$, $200 \leq D_A \leq 600$, and $30 \leq n_A \leq 70$, respectively,

L_B, D_B, n₁, n₂, n₃, and n_B for said diaryl carbonate purifying column B satisfy the following formulae; $1500 \leq L_B \leq 3000$, $150 \leq D_B \leq 500$, $7 \leq n_1 \leq 15$, $12 \leq n_2 \leq 30$, $3 \leq n_3 \leq 10$, and $25 \leq n_B \leq 55$, respectively,

T_A is in a range of from 190 to 240°C, P_A is in a range of from 2000 to 15000

P_A , T_B is in a range of from 190 to 240°C, and P_B is in a range of from 2000 to 15000 Pa.

4. The process according to any one of claims 1 to 3, wherein each of said
5 reactive distillation column, said high boiling point material separating column A and
said diaryl carbonate purifying column B is a distillation column having a tray and/or
a packing as said internal.

5. The process according to any one of claims 1 to 4, wherein said reactive
10 distillation column is a distillation column having, as the internal, the packing in the
upper portion of the column, and the tray in the lower portion of the column, and the
internal of each of said high boiling point material separating column A and said
diaryl carbonate purifying column B is the packing.

15 6. The process according to claim 5, wherein the packing is a structured
packing which is at least one selected from the group consisting of Mellapak,
Gempak, TECHNO-PAK, FLEXI-PAK, a Sulzer packing, a Goodroll packing, and a
Glitchgrid.

20 7. The process according to claim 4 or 5, wherein said tray of said reactive
distillation column is a sieve tray having a sieve portion and a down comer portion.

8. The process according to claim 7, wherein said sieve tray has 100 to
1000 holes / m² in the sieve portion.

25 9. The process according to claim 7 or 8, wherein the cross-sectional area

per hole of said sieve tray is in a range of from 0.5 to 5 cm².

10. A high-purity diphenyl carbonate which is a diaryl carbonate produced by the process according to any one of claims 1 to 9, said diphenyl carbonate being
5 unsubstituted or substituted with a lower hydrocarbon, and having a halogen content of not more than 0.1 ppm, and a content of by-products having a higher boiling point than that of said diphenyl carbonate of not more than 100 ppm.

11. The high-purity diphenyl carbonate according to claim 10, wherein said
10 diphenyl carbonate is unsubstituted diphenyl carbonate, and the halogen content is not more than 10 ppb, and the content of each of phenyl salicylate, xanthone, phenyl methoxybenzoate, and 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene, which are the by-products having the higher boiling point than that of the diphenyl carbonate, is not more than 30 ppm.

12. The high-purity diphenyl carbonate according to claim 11, wherein the
content of the by-products having the higher boiling point than that of the diphenyl carbonate is not more than 50 ppm.

13. The high-purity diphenyl carbonate according to claim 12, wherein the
20 halogen content is not more than 1 ppb, and the content of the by-products having the higher boiling point than that of the diphenyl carbonate is not more than 10 ppm.

14. An apparatus for producing a high-purity diaryl carbonate which
25 comprises;

a reactive distillation column comprising a continuous multi-stage distillation

column in which a homogeneous catalyst is present, said reactive distillation column receiving a reaction mixture containing an alkyl aryl carbonate as a starting material, which has been obtained through a transesterification reaction between a dialkyl carbonate and an aromatic monohydroxy compound, wherein a transesterification
5 reaction and distillation simultaneously is carried out in the column, a low boiling point reaction mixture containing a produced dialkyl carbonate is withdrawn from an upper portion of the column in a gaseous form, and a high boiling point reaction mixture containing a diaryl carbonate is withdrawn from a lower portion of the column in a liquid form;

10 a high boiling point material separating column A connected with said reactive distillation column and receiving said high boiling point reaction mixture, wherein separation and distillation is carried out into a column top component A_T containing the diaryl carbonate and a column bottom component A_B containing the catalyst; and

15 a diaryl carbonate purifying column B which is provided with a side cut outlet, and which is connected with said high boiling point material separating column A and receiving the column top component A_T from the side cut outlet, wherein separation and distillation is carried out into a column top component B_T , a side cut component B_S and a column bottom component B_B ; wherein

20 (a) said reactive distillation column comprises a continuous multi-stage distillation column having a length L (cm), an inside diameter D (cm), an internal with a number of stages n thereinside, a gas outlet having an inside diameter d_1 (cm) at the top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_2 (cm) at the bottom of the column or in a lower
25 portion of the column near to the bottom, at least one inlet provided in the upper portion and/or a middle portion of the column below the gas outlet, and at least one

inlet provided in the lower portion of the column above the liquid outlet, wherein L , D , n , d_1 , and d_2 satisfy the following formulae (1) to (6);

$$1500 \leq L \leq 8000 \quad (1)$$

$$100 \leq D \leq 2000 \quad (2)$$

$$5 \quad 2 \leq L/D \leq 40 \quad (3)$$

$$10 \leq n \leq 80 \quad (4)$$

$$2 \leq D/d_1 \leq 15 \quad (5)$$

$$5 \leq D/d_2 \leq 30 \quad (6);$$

(b) said high boiling point material separating column A comprises a
 10 continuous multi-stage distillation column having a length L_A (cm), an inside diameter D_A (cm), and an internal with a number of stages n_A thereinside, wherein L_A , D_A , and n_A satisfy the following formulae (7) to (9);

$$800 \leq L_A \leq 3000 \quad (7)$$

$$100 \leq D_A \leq 1000 \quad (8)$$

$$15 \quad 20 \leq n_A \leq 100 \quad (9);$$

(c) said diaryl carbonate purifying column B comprises a continuous
 multi-stage distillation column having a length L_B (cm), an inside diameter D_B (cm),
 an internal thereinside, an inlet B1 at an intermediate portion of the column, and a
 side cut outlet B2 between the inlet B1 and the column bottom, in which a number of
 20 stages of the internal above the inlet B1 is n_1 , a number of stages of the internals
 between the inlet B1 and the side cut outlet B2 is n_2 , a number of stages of the
 internals below the side cut outlet B2 is n_3 , and a total number of stages is $n_B (= n_1 +$
 $n_2 + n_3)$, wherein L_B , D_B , n_1 , n_2 , n_3 , and n_B satisfy the following formulae (10) to (15);

$$1000 \leq L_B \leq 5000 \quad (10)$$

$$25 \quad 100 \leq D_B \leq 1000 \quad (11)$$

$$5 \leq n_1 \leq 20 \quad (12)$$

$$12 \leq n_2 \leq 40 \quad (13)$$

$$3 \leq n_3 \leq 15 \quad (14)$$

$$20 \leq n_B \leq 70 \quad (15).$$

5 15. The apparatus according to claim 14, wherein a distillation operation of said high boiling point material separating column A is carried out at a column bottom temperature T_A in a range of from 185 to 280°C, and at a column top pressure P_A in a range of from 1000 to 20000 Pa, and a distillation operation of said diaryl carbonate purifying column B is carried out at a column bottom temperature T_B in a
10 range of from 185 to 280°C, and at a column top pressure P_B in a range of from 1000 to 20000 Pa.

 16. The apparatus according to claim 14 or 15, wherein L , D , L/D , and n for said reactive distillation column satisfy the following formulae; $2000 \leq L \leq$
15 6000 , $150 \leq D \leq 1000$, $3 \leq L/D \leq 30$, and $15 \leq n \leq 60$, respectively,

L_A , D_A , and n_A for said high boiling point material separating column A satisfy the following formulae; $1000 \leq L_A \leq 2500$, $200 \leq D_A \leq 600$, and $30 \leq n_A \leq 70$, respectively,

L_B , D_B , n_1 , n_2 , n_3 , and n_B for said diaryl carbonate purifying column B satisfy
20 the following formulae; $1500 \leq L_B \leq 3000$, $150 \leq D_B \leq 500$, $7 \leq n_1 \leq 15$, $12 \leq n_2 \leq 30$, $3 \leq n_3 \leq 10$, and $25 \leq n_B \leq 55$, respectively,

T_A is in a range of from 190 to 240°C, P_A is in a range of from 2000 to 15000 Pa, T_B is in a range of from 190 to 240°C, and P_B is in a range of from 2000 to 15000 Pa.

25

17. The apparatus according to any one of claims 14 to 16, wherein each

of said reactive distillation column, said high boiling point material separating column A and said diaryl carbonate purifying column B is a distillation column having a tray and/or a packing as said internal.

5 18. The apparatus according to any one of claims 14 to 17, wherein said reactive distillation column is a distillation column having, as the internal, the packing in the upper portion of the column, and the tray in the lower portion of the column, and the internal of each of said high boiling point material separating column A and said diaryl carbonate purifying column B is the packing.

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19. The apparatus according to claim 18, wherein the packing is a structured packing which is at least one selected from the group consisting of Mellapak, Gempak, TECHNO-PAK, FLEXI-PAK, a Sulzer packing, a Goodroll packing, and a Glitchgrid.

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20. The apparatus according to claim 17 or 18, wherein said tray of said reactive distillation column is a sieve tray having a sieve portion and a down comer portion.

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21. The apparatus according to claim 20, wherein said sieve tray has 100 to 1000 holes / m² in the sieve portion.

22. The apparatus according to claim 20 or 21, wherein the cross-sectional area per hole of said sieve tray is in a range of from 0.5 to 5 cm².

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