

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 that has been
10 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, and then subjecting a high boiling point reaction mixture containing a diaryl carbonate thus obtained to separation and purification using three continuous multi-stage distillation columns, each of which has a specified
15 structure.

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 a dialkyl carbonate and an aromatic
15 monohydroxy compound is also known. However, such transesterification reactions are all equilibrium reactions. The equilibrium is biased extremely toward the original system and the reaction rate is slow, and hence there are many difficulties in producing aromatic carbonates industrially using this method. Two types of proposals have been made to improve on the above difficulties.

20 These are developments of a catalyst to increase the reaction rate, and attempts to devise a reaction system so as to shift the equilibrium toward the product system as much as possible and thus improve the aromatic carbonate yield. For example, for the reaction between dimethyl carbonate and phenol, there have been proposed a process in which methanol produced as a by-product is distilled off by
25 azeotropy together with an azeotrope-forming agent, a process in which the methanol produced as a by-product is removed by being adsorbed onto a molecular

sieve, and a process 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 unreacted starting material that evaporates is separated off by distillation (see Patent Document 1:

5 Examples in Japanese Patent Application Laid-Open No. 56-123948 (corresponding to U.S. Patent No. 4182726)).

However, these reaction systems have basically been batch system or switchover system. Because there are limitations in the improvement of the reaction rate through catalyst development for such transesterification reactions, and
10 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 reaction rate being slow, and a gas-liquid interface in the reactor being small, based
15 on the volume of the liquid. Hence it is not possible to make the conversion high. Accordingly, it is difficult to attain the object of producing an aromatic carbonate continuously in large amounts stably for a prolonged period of time by means of the above methods, and many issues remain to be resolved before economical industrial implementation is possible.

20 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 a transesterification reaction, for example, a reactive distillation method in which a
25 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 continuously withdrawing a component containing a produced alkyl aryl carbonate from a lower portion of the column (see Patent Document 2: 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, 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 3: 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 4: 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 5: Japanese Patent Application Laid-Open No. 4-224547; Patent Document 6: Japanese Patent Application Laid-Open No. 4-230242; Patent Document 7: 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 Document 8: International Publication No. 00/18720 (corresponding to U.S. Patent No. 5362901); Patent Document 9: Italian Patent No. 01255746; Patent Document 10: Japanese Patent Application Laid-Open No. 6-9506 (corresponding to European Patent No. 0560159, and U.S. Patent No. 5282965); Patent Document 11: Japanese Patent Application Laid-Open No. 6-41022 (corresponding to European Patent No. 0572870, and U.S. Patent No. 5362901); Patent Documents 12: Japanese Patent Application Laid-Open No. 6-157424 (corresponding to European Patent No. 0582931, and U.S. Patent No. 5334742); Patent Document 13: Japanese Patent Application Laid-Open No. 6-184058 (corresponding to European Patent No. 0582930, and U.S. Patent No. 5344954); Patent Document 14: Japanese Patent Application Laid-Open No. 7-304713; Patent Document 15: Japanese Patent Application Laid-Open No. 9-40616; Patent Document 16: Japanese Patent Application Laid-Open No. 9-59225; Patent Document 17: Japanese Patent Application Laid-Open No. 9-110805; Patent Document 18: Japanese Patent Application Laid-Open No. 9-165357; Patent Document 19: Japanese Patent Application Laid-Open No. 9-173819; Patent Document 20: Japanese Patent Application Laid-Open No. 9-176094; Patent Document 21: Japanese Patent Application Laid-Open No. 2000-191596; Patent Document 22: Japanese Patent Application Laid-Open No. 2000-191597; Patent Document 23: Japanese Patent Application Laid-Open No. 9-194436 (corresponding to European Patent No. 0785184, and U.S. Patent No. 5705673); Patent Document 24: International Publication No. 00/18720 (corresponding to U.S. Patent No. 6093842); Patent Document 25: International Publication No. 01/042187

(corresponding to Published Japanese Translation of PCT Application No. 2003-516376); Patent Document 26: Japanese Patent Application Laid-Open No. 2001-64234; Patent Document 27: Japanese Patent Application Laid-Open No. 2001-64235; Patent Document 28: International Publication No. 02/40439

5 (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

10 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 Document 29: 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

15 aromatic hydroxy compound in the reaction system to a catalyst metal at not more than 2.0 (see Patent Document 30: 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

20 process is used as a starting material, and diphenyl carbonate can be produced by 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 31: Japanese Patent Application Laid-Open No. 9-255772 (corresponding to European Patent No. 0892001, and U.S. Patent No. 5747609)).

25 However, in all of these prior art documents in which the production of 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. not less than 1 ton / hr), nor is there any description suggesting such a process or apparatus. For example, the descriptions regarding the heights (H_1 and H_2 : cm), the diameters (D_1 and D_2 : cm), the numbers of stages (N_1 and N_2), and the feeding rates of the starting material (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

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	4
350	2.8	-	0.2	305	5~10	15+ PACKING	0.6	12
500	5	50	0.6	400	8	50	0.6	15
100	4	-	1.4	200	4	-	0.8	16
300	5	40	1.5	-	5	25	0.7	20
1200	20	40	86	600	25	20	31	29 30
600	-	20	66	600	-	20	22	31

In other words, the biggest pairs of continuous multi-stage distillation columns used when carrying out this reaction using a reactive distillation system are those disclosed by the present applicants in Patent Documents 30 and 31. 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 $H_1 = 1200$ cm, $H_2 = 600$ cm, $D_1 = 20$ cm, $D_2 = 25$ cm, $N_1 = N_2 = 50$ (Patent Document 15),

$Q_1 = 86 \text{ kg / hr}$, and $Q_2 = 31 \text{ kg / hr}$, and the amount of diphenyl carbonate produced has not exceeded approximately 6.7 kg / hr , which is not an amount produced on an industrial scale.

As methods for separating a diaryl carbonate from the reaction mixture containing the diaryl carbonate that has been produced through transesterification reaction and the like between a dialkyl carbonate and an aromatic monohydroxy compound as a starting material as described above, and then purifying the diaryl 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 diaryl 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 2 of Patent Document 10);

15 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
20 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 33: Example 1 in Japanese Patent Application Laid-open No. 4-100824; Patent Document 34: Japanese Patent Application Laid-open No. 9-169704); and

25 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
5 Patent Document 17).

Another is a method in which the diaryl 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
10 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 obtained as a column bottom component (see Patent Document 26).

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

15 V) a method in which the reaction mixture containing the catalyst is introduced into a third reactive distillation column, and further reaction and distillation are carried out, whereby the diphenyl carbonate is obtained as a side cut component from the reactive distillation column (see Patent Documents 12 and 13);

VI) a method in which the reaction mixture containing the catalyst is
20 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 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 30 and 31; Patent Document 35:
25 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

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 36: Japanese Patent 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 32: Japanese Patent Application Laid-open No. 9-194437 (corresponding to European Patent No. 0784048)).

However, it has been shown that various problems remain with such diaryl 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 on an industrial scale. Regarding the above II), the method of Patent Document 33 is a batch method, and the diphenyl carbonate which was obtained through the method disclosed in Patent Document 34 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 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, which is

undesirable. In actual fact, the diphenyl carbonate obtained in Example 1 in Patent Document 17 contains approximately 300 ppm of high boiling point by-products.

The process of the above IV in which the diphenyl carbonate is obtained from the bottom of the column is unsuitable since the purity is low and hence a desired

5 polycarbonate cannot be produced.

Since with the process of the above V, a reaction mixture containing all of the catalyst, unreacted starting material and impurities from the bottom of the 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 outlet
10 of the third reactive distillation column, vapor or mist of the starting material, the impurities, the catalyst or the like may thus be entrained, and hence the purity of the diphenyl carbonate obtained is low. The processes of the above VI and VII are preferable processes, but there is no mention of the presence of intermediate boiling point impurities having a boiling point between the alkyl aryl carbonate and the diaryl
15 carbonate. Moreover, with the process 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 32), nothing is mentioned 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 process for
20 diphenyl carbonate containing chlorinated impurities, nothing is mentioned 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 process, such chlorinated impurities are not separated out sufficiently, and hence
25 it is not be possible to use the diphenyl carbonate as a raw material for a polycarbonate. This is obvious from the fact that the chlorine content is 30 ppb in

the diphenyl carbonate (in which after washing with alkaline hot water, and with hot water, and then water and the lower boiling point material is removed by distillation, the resulting diphenyl carbonate not containing water is purified by distillation) obtained in Comparative Example 1 of Patent Document 37 (Japanese Patent Application Laid-open No. 11-12230: this application was filed more than one year after Patent Document 32), which discloses the similar purifying method as the above process.

Furthermore, in Patent Document 32, 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 this test method cannot evaluate whether the diphenyl carbonate is suitable for polymerization. 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 32, 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 32. Moreover, the purified amount of diphenyl carbonate disclosed in Patent Document 32 is 0.57 kg / hr, which is not on an industrial scale.

A reaction mixture obtained as a column bottom component by taking 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, continuously feeding this starting material into a reactive distillation column comprising a continuous multi-stage distillation column in which a homogeneous catalyst is present, and carrying out a transesterification reaction and distillation simultaneously in the column generally contains small amounts of various reaction by-products in addition to the diaryl carbonate, the starting material and the catalyst. Such by-products are known to include by-products having a lower boiling point than that of the aromatic monohydroxy compound used as a starting material such as an alkyl aryl ether (e.g. anisole), and by-products having a higher boiling point than that of the diaryl carbonate such as an aryloxy carbonyl-(hydroxy)-arene (e.g. phenyl salicylate) and an aryloxy carbonyl-(aryloxy carbonyl)-arene, and processes for separating these out have been proposed. For example, processes for separating out anisole (see Patent Documents 16, 17 and 20), and processes for separating out phenyl salicylate (see Patent Documents 32 and 36) have been proposed.

By carrying out more detailed studies on processes for the continuous production of the diaryl carbonate, the present inventors have discovered that in

addition to these publicly known impurities, intermediate boiling point by-products having a boiling point between the alkyl aryl carbonate and the diaryl carbonate are also present. Hitherto, there have been no documents whatsoever disclosing the presence of such intermediate boiling point by-products or a process for removing
5 the same.

When a diaryl carbonate for which the amounts of such intermediate boiling point by-products and high boiling point by-products have not been reduced down to a sufficient level is used as the raw material of a transesterification method polycarbonate, it has been discovered that these intermediate boiling point
10 by-products and high boiling point by-products cause discoloration and a deterioration in the properties of the polycarbonate produced. It is thus necessary to reduce the amounts of both intermediate boiling point by-products and high boiling point by-products as much as possible. Accordingly, there is need for a process that enables a high-purity diaryl carbonate having low contents of both intermediate
15 boiling point by-products and high boiling point by-products as required for producing a high-quality and high-performance aromatic polycarbonate to be produced stably for a prolonged period of time on an industrial scale of not less than 1 ton / hr.

Disclosure of Invention

20 It is an object of the present invention to provide 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 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
25 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 a continuous multi-stage distillation column, various proposals regarding processes for the production of reaction mixtures containing aromatic carbonates by means of a reactive distillation method have been made. However, these have all been on a small scale and 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 of a high-purity diaryl carbonate that can be used as a raw material of a high-quality and high-performance polycarbonate. Thus, the present inventors carried out studies aimed at discovering a specific process enabling a high-purity diaryl carbonate 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, the present invention provides:

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 that 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 said 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, wherein the improvement comprises:

at least three continuous multi-stage distillation columns comprising:

(a) a high boiling point material separating column A comprising 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 (1) to (3);

$$800 \leq L_A \leq 3000 \quad (1)$$

$$100 \leq D_A \leq 1000 \quad (2)$$

$$20 \leq n_A \leq 100 \quad (3),$$

(b) a diaryl carbonate purifying column B comprising a continuous multi-stage distillation column having a side cut outlet, a length L_B (cm), an inside diameter D_B (cm), and an internal with a number of stages n_B therein, wherein L_B , D_B , and n_B satisfy the following formulae (4) to (6);

$$1000 \leq L_B \leq 5000 \quad (4)$$

$$100 \leq D_B \leq 1000 \quad (5)$$

$$20 \leq n_B \leq 70 \quad (6), \text{ and}$$

(c) an intermediate boiling point material separating column C comprising a continuous multi-stage distillation column having a side cut outlet, a length L_C (cm), an inside diameter D_C (cm), and an internal with a number of stages n_C therein, wherein L_C , D_C , and n_C satisfy the following formulae (7) to (9);

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

$$50 \leq D_C \leq 500 \quad (8)$$

$$10 \leq n_C \leq 50 \quad (9),$$

wherein said three continuous multi-stage distillation columns are arranged in this order.

2. The process according to item 1, wherein not less than 1 ton / hr of the high-purity diaryl carbonate is obtained continuously as a side cut component B_S

from said diaryl carbonate purifying column B.

3. The process according to item 1 or 2, wherein said high boiling point reaction mixture containing the diaryl carbonate continuously withdrawn from the lower portion of said reactive distillation column in a liquid form is:

5 (a) continuously introduced into said high boiling point material separating column A, and continuously subjected to 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 a high boiling point material,

(b) said column top component A_T is continuously introduced into said diaryl carbonate purifying column B, and continuously subjected to separation by distillation
10 into a column top component B_T , the side cut component B_S , and a column bottom component B_B , and

(c) said column top component B_T is continuously introduced into said intermediate boiling point material separating column C, and continuously subjected
15 to separation by distillation into a column top component C_T containing the alkyl aryl carbonate, a side cut component C_S containing an intermediate boiling point material having a boiling point between that of the alkyl aryl carbonate and that of the diaryl carbonate, and a column bottom component C_B containing the diaryl carbonate.

4. The process according to any one of items 1 to 3, wherein the column top
20 component C_T from said intermediate boiling point material separating column C is continuously fed into said reactive distillation column.

5. The process according to any one of items 1 to 4, wherein the column bottom component C_B from said intermediate boiling point material separating column C is continuously fed into said high boiling point material separating column A.

25 6. The process according to any one of items 1 to 5, wherein said reactive distillation column comprises a continuous multi-stage distillation column having a

length L (cm), an inside diameter D (cm), and an internal with a number of stages n therein, and having 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 (10) to (15):

$$1500 \leq L \leq 8000 \quad (10)$$

$$100 \leq D \leq 2000 \quad (11)$$

$$2 \leq L/D \leq 40 \quad (12)$$

$$10 \leq n \leq 80 \quad (13)$$

$$2 \leq D/d_1 \leq 15 \quad (14)$$

$$5 \leq D/d_2 \leq 30 \quad (15).$$

7. The process according to any one of items 1 to 6, wherein said diaryl carbonate purifying column B comprises a continuous multi-stage distillation column having an inlet B1 at a middle portion of the column, a side cut outlet B2 between said inlet B1 and the column bottom, and having a number of stages n_1 of an internal above the inlet B1, a number of stages n_2 of an internal between the inlet B1 and the side cut outlet B2, and a number of stages n_3 of an internal below the side cut outlet B2, the total number of stages ($n_1 + n_2 + n_3$) being n_B , wherein n_1 , n_2 , and n_3 satisfy the following formulae (16) to (18):

$$5 \leq n_1 \leq 20 \quad (16)$$

$$12 \leq n_2 \leq 40 \quad (17)$$

$$3 \leq n_3 \leq 15 \quad (18).$$

8. The process according to any one of items 1 to 7, wherein said intermediate

boiling point material separating column C comprises a continuous multi-stage distillation column having an inlet C1 at a middle portion of the column, a side cut outlet C2 between said inlet C1 and the column bottom, and having a number of stages n_4 of an internal above the inlet C1, a number of stages n_5 of an internal
 5 between the inlet C1 and the side cut outlet C2, and a number of stages n_6 of an internal below the side cut outlet C2, the total number of stages ($n_4 + n_5 + n_6$) being n_C , wherein n_4 , n_5 , and n_6 satisfy the following formulae (19) to (21):

$$2 \leq n_4 \leq 15 \quad (19)$$

$$5 \leq n_5 \leq 30 \quad (20)$$

$$10 \quad 3 \leq n_6 \leq 20 \quad (21).$$

9. The process according to any one of items 1 to 8, wherein each of said reactive distillation column, said high boiling point material separating column A, said diaryl carbonate purifying column B, and said intermediate boiling point material separating column C comprises a distillation column having a tray and/or a packing as the
 15 internal.

10. The process according to item 9, wherein said reactive distillation column comprises 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, said diaryl
 20 carbonate purifying column B and said intermediate boiling point material separating column C is the packing.

11. The process according to item 9 or 10, wherein said packing is a structured packing of at least one type selected from the group consisting of Mellapak, Gempak, TECHNO-PAK, Flexipac, a Sulzer packing, a Goodroll packing, and a Glitchgrid.

25 12. The process according to item 9 or 10, wherein said tray in said reactive distillation column is a sieve tray having a sieve portion and a down comer portion.

13. The process according to item 12 wherein said sieve tray has 100 to 1000 holes / m² in the sieve portion.
14. The process according to item 12 or 13, wherein the cross-sectional area per hole of said sieve tray is in a range of from 0.5 to 5 cm².
- 5 15. The process according to any one of items 1 to 14, wherein 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 a column top pressure P_A in a range of from 1000 to 20000 Pa.
16. The process according to any one of items 1 to 15, wherein distillation
10 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 a column top pressure P_B in a range of from 1000 to 20000 Pa.
17. The process according to any one of items 1 to 16, wherein distillation
15 operation of said intermediate boiling point material separating column C is carried out at a column bottom temperature T_C in a range of from 150 to 280°C, and a column top pressure P_C in a range of from 500 to 18000 Pa.
18. The process according to any one of items 1 to 17, wherein a reflux ratio for said high boiling point material separating column A is in a range of from 0.01 to 10.
19. The process according to any one of items 1 to 18, wherein a reflux ratio for
20 said diaryl carbonate purifying column B is in a range of from 0.01 to 10.
20. The process according to any one of items 1 to 19, wherein a reflux ratio for said intermediate boiling point material separating column C is in a range of from 0.01 to 10.
21. A high-purity diphenyl carbonate that is a diaryl carbonate produced by the
25 process according to any one of items 1 to 20, the diphenyl carbonate being unsubstituted or substituted with a lower hydrocarbon, and having a halogen content

of not more than 0.1 ppm, a content of said intermediate boiling point material of not more than 100 ppm, and a content of by-products having a higher boiling point than that of the diphenyl carbonate of not more than 100 ppm.

22. The high-purity diphenyl carbonate according to item 21, wherein the diphenyl
5 carbonate is unsubstituted diphenyl carbonate, and the halogen content is not more than 10 ppb, the content of said intermediate boiling point material is not more than 30 ppm, and the content of each of phenyl salicylate, xanthone, phenyl methoxybenzoate, and 1-phenoxybenzyl-2-phenoxybenzoate, which are the by-products having a higher boiling point than that of the diphenyl carbonate, is
10 not more than 30 ppm.

23. The high-purity diphenyl carbonate according to item 22, wherein the content of said intermediate boiling point material is not more than 10 ppm, and the content of the by-products having a higher boiling point than that of the diphenyl carbonate is not more than 50 ppm.

15 24. The high-purity diphenyl carbonate according to item 23, wherein the halogen content is not more than 1 ppb, and the content of the by-products having a higher boiling point than that of the diphenyl carbonate is not more than 10 ppm.

25. A process for the production of an aromatic polycarbonate, comprising using the high-purity diphenyl carbonate according to any one of items 21 to 24 as a raw
20 material for the production of an aromatic polycarbonate through transesterification with an aromatic dihydroxy compound.

26. An aromatic polycarbonate produced by the process according to item 25.

27. An apparatus for producing a high-purity diaryl carbonate in which the high-purity diaryl carbonate is produced by taking as a starting material a reaction
25 mixture containing an alkyl aryl carbonate that 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 said 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, the apparatus comprising:

(a) a high boiling point material separating column A comprising 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 (1) to (3);

$$800 \leq L_A \leq 3000 \quad (1)$$

$$100 \leq D_A \leq 1000 \quad (2)$$

$$20 \leq n_A \leq 100 \quad (3),$$

(b) a diaryl carbonate purifying column B which is connected said high boiling point material separating column A, and which comprises a continuous multi-stage distillation column having a side cut outlet, a length L_B (cm), an inside diameter D_B (cm), and an internal with a number of stages n_B therein, wherein L_B , D_B , and n_B satisfy the following formulae (4) to (6);

$$1000 \leq L_B \leq 5000 \quad (4)$$

$$100 \leq D_B \leq 1000 \quad (5)$$

$$20 \leq n_B \leq 70 \quad (6), \text{ and}$$

(c) an intermediate boiling point material separating column C which is connected to said diaryl carbonate purifying column B, and which comprises a continuous multi-stage distillation column having a side cut outlet, a length L_C (cm),

an inside diameter D_c (cm), and an internal with a number of stages n_c therein, wherein L_c , D_c , and n_c satisfy the following formulae (7) to (9);

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

$$50 \leq D_c \leq 500 \quad (8)$$

$$10 \leq n_c \leq 50 \quad (9).$$

28. The apparatus according to item 27, wherein said reactive distillation column comprises a continuous multi-stage distillation column having a length L (cm), an inside diameter D (cm), and an internal with a number of stages n therein, and having 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 (10) to (15):

$$1500 \leq L \leq 8000 \quad (10)$$

$$100 \leq D \leq 2000 \quad (11)$$

$$2 \leq L / D \leq 40 \quad (12)$$

$$10 \leq n \leq 80 \quad (13)$$

$$2 \leq D / d_1 \leq 15 \quad (14)$$

$$5 \leq D / d_2 \leq 30 \quad (15).$$

29. The apparatus according to item 27 or 28, wherein said diaryl carbonate purifying column B comprises a continuous multi-stage distillation column having an inlet B1 at a middle portion of the column, a side cut outlet B2 between said inlet B1 and the column bottom, and having a number of stages n_1 of an internal above the inlet B1, a number of stages n_2 of an internal between the inlet B1 and the side cut

outlet B2, and a number of stages n_3 of an internal below the side cut outlet B2, the total number of stages ($n_1 + n_2 + n_3$) being n_B , wherein n_1 , n_2 , and n_3 satisfy the following formulae (16) to (18):

$$5 \leq n_1 \leq 20 \quad (16)$$

$$12 \leq n_2 \leq 40 \quad (17)$$

$$3 \leq n_3 \leq 15 \quad (18).$$

30. The apparatus according to any one of items 27 to 29, wherein said intermediate boiling point material separating column C comprises a continuous multi-stage distillation column having an inlet C1 at a middle portion of the column, a side cut outlet C2 between said inlet C1 and the column bottom, and having a number of stages n_4 of an internal above the inlet C1, a number of stages n_5 of an internal between the inlet C1 and the side cut outlet C2, and a number of stages n_6 of an internal below the side cut outlet C2, the total number of stages ($n_4 + n_5 + n_6$) being n_C , wherein n_4 , n_5 , and n_6 satisfy the following formulae (19) to (21):

$$2 \leq n_4 \leq 15 \quad (19)$$

$$5 \leq n_5 \leq 30 \quad (20)$$

$$3 \leq n_6 \leq 20 \quad (21).$$

Advantageous Effects of the Invention

20 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 / 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 obtained through a transesterification

reaction between a dialkyl carbonate and an aromatic monohydroxy compound.

Brief Description of Drawings

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

FIG. 2 is a schematic view of a high-purity diaryl carbonate production apparatus for carrying out the present invention in which the reactive distillation column, a high boiling point material separating column A, a diaryl carbonate purifying column B, and an intermediate boiling point material separating column C are connected together; each of these continuous multi-stage distillation columns has installed therein an internal having the predetermined number of stages.

1: gas outlet; 2: liquid outlet; 3 and 4: inlet; 5: end plate; L: trunk portion (cm); D: inside diameter of trunk portion (cm); d_1 : inside diameter of gas inlet (cm); d_2 : inside diameter of liquid outlet (cm); 101, A1, B1, C1: inlet; B2 and C2: side cut outlet; 106: column top component (low boiling point reaction mixture) outlet of reactive distillation column; 111: column bottom component (high boiling point reaction mixture) outlet of reactive distillation column; 103, 13, 23, 43: column top gas outlet; 104, 14, 24, 44, 108, 18, 28, 38, 48: heat exchanger; 105, 15, 25, 45: reflux liquid inlet; 16: column top component (A_T) outlet of high boiling point material separating column A; 11: column bottom component (A_B) outlet of high boiling point material separating column A; 107, 17, 27, 47: column bottom liquid outlet; 26: column top component (B_T) outlet of diaryl carbonate purifying column B; 31: column bottom component (B_B) outlet of diaryl carbonate purifying column B; 33: side cut component (B_S) outlet of diaryl carbonate purifying column B; 46: column top component (C_T) outlet of intermediate boiling point material separating column C; 51: column bottom component (C_B) outlet of intermediate boiling point material separating column C; 53:

side cut component (C_s) outlet of intermediate boiling point material separating column C.

Best Mode for Carrying Out the Invention

5 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 (22);



wherein R¹ represents an alkyl group having 1 to 10 carbon atoms, an alicyclic group
10 having 3 to 10 carbon atoms, or an aralkyl group having 6 to 10 carbon atoms.

Examples of R¹ 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
15 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.

20 Examples of dialkyl carbonates having such R¹ 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
25 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).

5 Of these dialkyl carbonates, ones preferably used in the present invention
 are dialkyl carbonates in which R¹ 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
 10 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 undermentioned general formula (23). The type of the
 aromatic monohydroxy compound is not limited, so long as the hydroxyl group is
 15 directly bonded to the aromatic group;



 wherein Ar¹ represents an aromatic group having 5 to 30 carbon atoms. Examples
 of aromatic monohydroxy compounds having such an Ar¹ include phenol; various
 alkylphenols such as cresol (isomers), xlenol (isomers), trimethylphenol (isomers),
 20 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
 25 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 phenol and substituted phenols in which Ar¹ is an aromatic group having 6 to 10 carbon atoms. Unsubstituted phenol is particularly preferable. Moreover, of these aromatic monohydroxy compounds, ones substantially not containing a halogen are preferably used in the present invention.

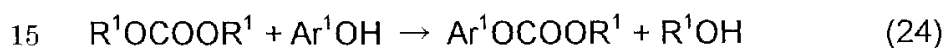
The molar ratio of the dialkyl carbonate to the aromatic monohydroxy compound used for obtaining a reaction mixture containing an alkyl aryl carbonate that is the starting material in the present invention must be in a range of from 0.1 to 10. Outside this range, the amount of unreacted material remaining 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 this unreacted material. For such reasons, the above molar ratio is preferable in a range of from 0.5 to 5, 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 phenyl carbonates, diphenyl 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 aromatic monohydroxy compounds, the reaction liquid and the like.

In the present invention, it is particularly preferable to use a starting material
 5 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 for this is that 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
 10 inhibits the polymerization reaction, and cause a deterioration in the properties of the polycarbonate produced, and cause discoloration of the polycarbonate.

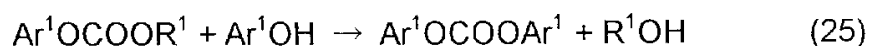
The reaction mixture containing the alkyl aryl carbonate is produced through a transesterification reaction between the dialkyl carbonate and the aromatic monohydroxy compound (formula 24).



The process for producing the reaction mixture containing the alkyl aryl carbonate may be any process, but one 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
 20 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 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
 25 column.

In the present invention, the reaction mixture containing the alkyl aryl

carbonate obtained in the above method is continuously fed into a reactive distillation column 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 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 (formula 25), and a reaction in which two molecules of the alkyl aryl carbonate are converted into the diaryl carbonate and the dialkyl carbonate through a transesterification reaction therebetween, i.e. a disproportionation reaction (formula 26). In the reactive distillation column of the present invention, it is mainly the disproportionation reaction of the alkyl aryl carbonate that occurs.



Note that 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 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 processes, for example alcohols, alkyl aryl ethers, the diaryl carbonates, intermediate boiling point by-products, and/or high boiling point by-products. A process in which the reaction mixture obtained through the transesterification reaction between the dialkyl carbonate and the aromatic monohydroxy compound is

taken as is as the starting material in the present invention without the unreacted materials and the catalyst being separated therefrom is also preferable. Moreover, in the case of industrial implementation as in the present invention, as the dialkyl carbonate and aromatic monohydroxy compound used for obtaining the reaction mixture containing the alkyl aryl carbonate that is taken as 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 processes.

The reactive distillation column used in the present invention preferably comprises 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. That is, 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. More specifically, the reactive distillation column preferably comprises a continuous multi-stage distillation column having a length L (cm), an inside diameter D (cm) and an internal with a number of stages n thereinside, and moreover having 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, d₁, and d₂ satisfy the following formulae (10) to (15):

$$1500 \leq L \leq 8000 \quad (10)$$

$$100 \leq D \leq 2000 \quad (11)$$

$$2 \leq L / D \leq 40 \quad (12)$$

$$10 \leq n \leq 80 \quad (13)$$

$$2 \leq D / d_1 \leq 15 \quad (14)$$

$$5 \leq D / d_2 \leq 30 \quad (15).$$

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.

It has been discovered that by using the continuous multi-stage distillation column that simultaneously satisfies the formulae (10) to (15), the high boiling point reaction mixture containing the diaryl carbonate as a main component 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 of not less than 1 ton / hr. Although the reason why it has become possible to produce a diaryl carbonate on an industrial scale with such excellent effects by implementing the process of the present invention is not clear, this is supposed to be due to a combined effect brought about when the conditions of the formulae (10) to (15) are combined. Preferable ranges for the respective factors

are described below.

If L (cm) is less than 1500, then the conversion decreases and it is not possible to attain the desired production amount. Moreover, to keep down the equipment cost while securing a conversion 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 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 becomes necessary to increase the temperature in the lower portion of the column, and hence side reactions become liable to occur, bringing about a decrease in the selectivity. A more 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 conversion decreases and it is not possible to attain the desired production amount. Moreover, to keep down the equipment cost while securing a conversion enabling the desired production amount to be 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 becomes necessary to increase the temperature in the lower portion of the column, and hence

side reactions become liable to occur, bringing about a decrease in 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,
 5 large amounts of gaseous components are readily released to the outside of the system, and hence stable operation becomes difficult. If D / d_1 is greater than 15, then the gaseous component withdrawal amount becomes relatively low, and hence stable operation becomes difficult, and moreover 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 $3 \leq$
 10 $D / d_1 \leq 10$ 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 becomes excessively fast, and hence erosion becomes liable to
 15 occur, 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.

The term "prolonged stable operation" used in the present invention means that operation can be carried out continuously in a steady state based on the operating conditions with no clogging of piping, erosion, or distillation abnormalities
 20 such as flooding for not less than 1000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours, and a prescribed amount of the diaryl carbonate can be produced while maintaining high selectivity.

The "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
 25 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 preferably comprises 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, an irregular packing 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, Goodroll packing or a Glitchgrid are preferable. Note that the term "number of stages (n) of the 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 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 the multi-stage distillation column having both the packing and the tray as the internal 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 for the reactive distillation column in the present invention, the sieve tray having a sieve portion and a down comer portion is particularly good as the tray of the internal in terms of the relationship between performance and equipment cost. It has also been discovered that the sieve tray preferably has 100 to 1000 holes / m^2 in the sieve portion. A more preferable number of holes is 120 to 900 holes / m^2 , yet more preferably 150 to 800 holes / m^2 . 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 cm^2 . A more preferable cross-sectional area per hole is 0.7 to 4 cm^2 , yet more preferably 0.9 to 3 cm^2 .

Furthermore, it has been discovered that it is particularly preferable if the sieve tray has 100 to 1000 holes / m^2 in the sieve portion, and the cross-sectional area per hole is in a range of from 0.5 to 5 cm^2 . 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, a Sulzer packings, a Goodroll packing, and a Glitchgrid, and the sieve tray has 100 to 1000 holes / m^2 in the sieve portion, and the cross-sectional area per hole is in a range of from 0.5 to 5 cm^2 .

It has been shown that by adding the above conditions to the reactive distillation column, the reactive distillation process in the present invention can be accomplished more easily.

When carrying out the reactive distillation process in the present invention, a 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 portion of the column in a gaseous form, and continuously withdrawing a high boiling point reaction mixture having the diaryl carbonate as a main reaction 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 be added as required. 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 from 0.005 to 10 % by weight, more preferably from 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 into 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 in which a reflux operation of
5 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 is preferable. In this case, the reflux ratio is generally in a range of from 0.05 to 10, preferably from 0.08 to 5, more preferably from 0.1 to 2.

10 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 a middle portion of the column below the gas outlet in the upper portion of the
15 distillation column. Moreover, in the case of using a distillation column having a packing portion in the upper portion thereof and a tray portion in the lower portion thereof, which is a preferable embodiment in 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
20 of structured packings, a process 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
25 of the internal in the 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 range of from 130 to 280°C, more preferably from 150 to 260°C, yet more preferably from 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 column top pressure is generally in a range of from 0.1 to 2×10^7 Pa, preferably from 10^3 to 10^6 Pa, more preferably from 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, an alkyl aryl ether, the aromatic monohydroxy compound, the alkyl aryl carbonate, by-products and so on in addition to the diaryl carbonate. Furthermore, this high boiling point reaction mixture generally contains small amounts of other impurities and reaction by-products, for example an intermediate boiling point material having a boiling point between that of the alkyl aryl carbonate and that of the diaryl carbonate such as cresol, an alkoxycarbonyl-(hydroxy)-arene (e.g. methyl salicylate), an alkyl-(alkylaryl)

carbonate (e.g. methyl cresyl carbonate), an alkoxycarbonyl-(alkoxycarboxyl)-arene (e.g. methyl methoxybenzoate), an alkoxyethyl-(aryl) carbonate (e.g. methoxyethyl-phenyl carbonate) and an alkylaryl-aryl ether (e.g. cresyl phenyl ether), and high boiling point material having a higher boiling point than that of the diaryl carbonate such as an aryloxy carbonyl-(hydroxy)-arene (e.g. phenyl salicylate), an alkoxycarbonyl-(aryloxy)-arene (e.g. methyl phenoxybenzoate), an alkylaryl-aryl carbonate (e.g. cresyl phenyl carbonate), xanthone and substituted xanthenes, an aryloxy carbonyl-(alkoxy)-arene (e.g. phenyl methoxybenzoate), an aryloxy carbonyl-(aryloxy)-arene (e.g. phenyl phenoxybenzoate) and an aryloxy carbonyl-(aryloxy carboxyl)-arene (e.g. 1-phenoxy carbonyl-2-phenoxy carboxy-phenylene).

The compounds in brackets for the intermediate boiling point material and the high boiling point material described above are compounds that may be present in the high boiling point reaction mixture containing diphenyl carbonate continuously withdrawn from the lower portion of the reactive distillation column in the case of using as the starting material a reaction mixture containing methyl phenyl carbonate obtained through a transesterification reaction between dimethyl carbonate and phenol. Moreover, the cause of the production of a compound having an alkoxyethyl group is unclear, but this may be due to a 2-alkoxyethanol and/or 2-alkoxyethyl alkyl carbonate present in a small amount in the dialkyl carbonate by-produced in the case that the dialkyl carbonate is produced from ethylene carbonate and an alcohol.

However, the high boiling point by-products as described above may be difficult to separate out, and with processes proposed hitherto, it has not been possible to reduce the amounts of such high boiling point by-products down to a sufficient level. Moreover, regarding the intermediate boiling point by-products, in

documents hitherto there has not even been any mention whatsoever of the existence thereof, and hence there have been no documents whatsoever disclosing or suggesting a process for separating out and thus removing such intermediate boiling point by-products. When producing a diaryl carbonate from a dialkyl carbonate and an aromatic monohydroxy compound, the present inventors have carried out prolonged continuous operation while recycling and thus reusing the starting material, and as a result have discovered that the intermediate boiling point material and the high boiling point material as described above are by-produced, and accumulate in the system over time. The present inventors have also ascertained that if a diaryl carbonate for which the amounts of such intermediate boiling point material and the high boiling point material have not been reduced down to a sufficient level is used as the raw material of a transesterification method polycarbonate, then this material will cause discoloration and a deterioration in properties. Accordingly, an efficient process for reducing the amounts of both the intermediate boiling point by-products and the high boiling point by-products down to a sufficient level is required. The process of the present invention attains this object.

In the present invention, the following must be carried out: the high boiling point reaction mixture containing the diaryl carbonate continuously withdrawn from the lower portion of the reactive distillation column is

- (a) continuously introduced into a high boiling point material separating column A, and continuously subjected to 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 a high boiling point material;
- (b) the column top component (A_T) is continuously introduced into a diaryl carbonate purifying column B having a side cut outlet, and continuously subjected to separation

by distillation into a column top component (B_T), a side cut component (B_S) and a column bottom component (B_B), high-purity diaryl carbonate being continuously withdrawn as the side cut component (B_S); and

- (c) the column top component (B_T) is continuously introduced into an intermediate boiling point material separating column C having a side cut outlet, and continuously subjected to separation by distillation into a column top component (C_T) having as a main component thereof the alkyl aryl carbonate, a side cut component (C_S) having as a main component thereof intermediate boiling point material having a boiling point between that of the alkyl aryl carbonate and that of the diaryl carbonate, and a column bottom component (C_B) having as a main component thereof the diaryl carbonate.

It is a characteristic feature of the present invention that the above processes (a), (b) and (c) are carried out in this order. This is because by carrying out these processes in this order, the heat history of the diaryl carbonate can be minimized, and as a result side reactions of the diaryl carbonate can be suppressed. With the process described in Patent Document 17 in which separation by distillation is carried out using three columns in order and the diaryl carbonate is obtained from the top of the third column, the heat history of the diaryl carbonate is great. In the present invention, it is more preferably to carry out the following:

- (d) the column top component (C_T) is continuously fed into the reactive distillation column; and/or
- (e) the column bottom component (C_B) is continuously fed into the high boiling point material separating column A.

By carrying out the process(es) of (d) and/or (e) for recycling and thus reusing the column top component (C_T) and/or the column bottom component (C_B), the productivity for the high-purity diaryl carbonate can be improved, which is very

important in the case of industrial implementation.

In the present invention, not less than 1 ton / hr of the high-purity diaryl carbonate is obtained continuously as the side cut component (B_S) from the diaryl carbonate purifying column B. For this purpose, the high boiling point material separating column A, the diaryl carbonate purifying column B and the intermediate boiling point material separating column C 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 in the order described above.

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 (1) to (3):

$$800 \leq L_A \leq 3000 \quad (1)$$

$$100 \leq D_A \leq 1000 \quad (2)$$

$$20 \leq n_A \leq 100 \quad (3).$$

The internal is preferably the tray and/or the packing as described above.

It is undesirable for L_A (cm) to be less than 800, since then the height over which internal can be installed becomes limited and hence the separation efficiency decreases. 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 $35 \leq n_A \leq 60$ being yet more preferable.

The distillation conditions for the high boiling point material 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.

It is undesirable for T_A to be lower 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 undesirable for T_A to be higher than 280°C, since then high boiling point by-products are produced during the distillation. 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 lower 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 higher than 20000 Pa, since then the distillation temperature must be 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.

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

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), and an internal with a number of stages n_B thereinside, wherein L_B , D_B , and n_B satisfy the following formulae (4) to (6):

$$1000 \leq L_B \leq 5000 \quad (4)$$

$$100 \leq D_B \leq 1000 \quad (5)$$

$$20 \leq n_B \leq 70 \quad (6).$$

The internal is preferably the tray and/or the packing as described above.

Furthermore, the diaryl carbonate purifying column B is preferably a continuous multi-stage distillation column having an inlet B1 at a middle portion of the column, and a side cut outlet B2 between the inlet B1 and the column bottom, and having a number of stages n_1 of the internal above the inlet B1, a number of stages n_2 of the internal between the inlet B1 and the side cut outlet B2, and a number of stages n_3 of the internal below the side cut outlet B2, the total number of stages ($n_1 + n_2 + n_3$) being n_B , wherein n_1 , n_2 , and n_3 satisfy the following formulae (16) to (18):

$$5 \leq n_1 \leq 20 \quad (16)$$

$$12 \leq n_2 \leq 40 \quad (17)$$

$$3 \leq n_3 \leq 15 \quad (18).$$

It is undesirable for L_B (cm) to be less than 1000, since then the height over which internal can be installed becomes limited and hence the separation efficiency decreases. 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 production amount. Moreover, to keep down the equipment cost while attaining the
 5 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 keep
 10 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
 15 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 diaryl 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 $3 \leq n_3 \leq$
 20 15 respectively. More preferable ranges are $7 \leq n_1 \leq 15$, $12 \leq n_2 \leq 30$, and $3 \leq n_3 \leq 10$.

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 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 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 190 to 240°C , with 195 to 230°C being yet more preferable.

5 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 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 2000 to 15000 Pa, with 3000 to 13000 Pa being yet more preferable.

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

The intermediate boiling point material separating column C must be a continuous multi-stage distillation column having a length L_C (cm), an inside diameter D_C (cm), and an internal with a number of stages n_C thereinside, wherein L_C , D_C , and n_C satisfy the following formulae (7) to (9):

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

$$50 \leq D_C \leq 500 \quad (8)$$

$$10 \leq n_C \leq 50 \quad (9).$$

20 The internal is preferably the tray and/or the packing as described above.

Furthermore, the intermediate boiling point material separating column C is preferably a continuous multi-stage distillation column having an inlet C1 at an intermediate stage of the column, and a side cut outlet C2 between the inlet C1 and the column bottom, and having a number of stages n_4 of the internal above the inlet C1, a number of stages n_5 of the internal between the inlet C1 and the side cut outlet C2, and a number of stages n_6 of the internal below the side cut outlet C2, the total

number of stages ($n_4 + n_5 + n_6$) being n_C , wherein n_4 , n_5 , and n_6 satisfy the following formulae (19) to (21):

$$2 \leq n_4 \leq 15 \quad (19)$$

$$5 \leq n_5 \leq 30 \quad (20)$$

$$5 \quad 3 \leq n_6 \leq 20 \quad (21).$$

It is undesirable for L_C (cm) to be less than 800, since then the height over which internal can be installed becomes limited and hence the separation efficiency decreases. Moreover, to keep down the equipment cost while attaining the desired separation efficiency, L_C must be made to be not more than 3000. A more
10 preferable range for L_C (cm) is $1000 \leq L_C \leq 2500$, with $1200 \leq L_C \leq 2000$ being yet more preferable.

If D_C (cm) is less than 50, 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_C must be made to be not more than 500. A more
15 preferable range for D_C (cm) is $80 \leq D_C \leq 300$, with $100 \leq D_C \leq 200$ being yet more preferable.

If n_C is less than 10, then the separation efficiency for the column as a whole decreases and hence the desired high purity cannot be attained. Moreover, to keep down the equipment cost while attaining the desired separation efficiency, n_C must
20 be made to be not more than 50. Furthermore, if n_C is greater than 50, then the pressure difference between the top and bottom of the column becomes too great, and hence prolonged stable operation of the intermediate boiling point material separating column C becomes difficult. Moreover, it becomes necessary to increase the temperature in the lower portion of the column, and hence side
25 reactions become liable to occur, which is undesirable. A more preferable range for n_C is $13 \leq n_C \leq 40$, with $16 \leq n_C \leq 30$ being yet more preferable.

Furthermore, it has been ascertained that to efficiently separate out intermediate boiling point material, and improve the productivity for the desired high-purity diaryl carbonate, it is preferable to n_4 , n_5 , and n_6 to be in the ranges $2 \leq n_4 \leq 15$, $5 \leq n_5 \leq 30$, and $3 \leq n_6 \leq 20$ respectively. More preferable ranges are $3 \leq n_4 \leq 10$, $7 \leq n_5 \leq 20$, and $4 \leq n_6 \leq 15$.

The distillation conditions for the intermediate boiling point material separating column C are preferably a column bottom temperature T_C in a range of from 150 to 280°C, and a column top pressure P_C in a range of from 500 to 18000 Pa.

It is undesirable for T_C to be less than 150°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 undesirable for T_C to be greater than 280°C, since then high boiling point by-products are produced during the distillation. A more preferable range for T_C is 160 to 240°C, with 165 to 230°C being yet more preferable.

It is undesirable for P_C to be less than 500 Pa, since then large equipment enabling a high vacuum to be maintained must be used. Moreover, it is undesirable for P_C to be greater than 18000 Pa, since then the distillation temperature must be increased and hence production of by-products increases. A more preferable range for P_C is from 800 to 15000 Pa, with from 1000 to 13000 Pa being yet more preferable.

Moreover, the reflux ratio for the intermediate boiling point material separating column C is generally in a range of from 0.01 to 10, preferably from 0.1 to 5, more preferably from 0.2 to 2.

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

boiling point material separating column C simultaneously satisfying all of the above necessary conditions, a high-purity diaryl carbonate can be produced on an industrial scale of not less than 1 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 (1) to (9) are combined.

In the present invention, the high boiling point reaction mixture continuously withdrawn from the bottom of the reactive distillation column is preferably fed into the high boiling point material separating column A. This high boiling point reaction mixture generally contains 0.05 to 2 % by weight of the dialkyl carbonate, 0.1 to 20 % by weight of the aromatic monohydroxy compound, 0.02 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, 0.01 to 1 % by weight of intermediate boiling point by-products, 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 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 will be approximately constant. Nevertheless, 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 the 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 depending on 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 not less than 1 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 depending on the size of the apparatus, the required production amount and so on, but is generally 200 ton / hr.

The high boiling point reaction mixture continuously fed into the high boiling point material separating column A is separated into a column top component (A_T)

comprising most of the diaryl carbonate, most of compounds having a lower boiling point than that of the diaryl carbonate such as unreacted starting material, an alkyl aryl ether, the alkyl aryl carbonate and an intermediate boiling point material, and a very small amount of high boiling point by-products, and a column bottom component

5 (A_B) containing a small amount of the diaryl carbonate, the catalyst, and most of by-products having a higher boiling point than that of the diaryl carbonate. The column bottom component (A_B) may contain small amounts of the aromatic monohydroxy compound, the alkyl aryl carbonate and the intermediate boiling point by-products. Such organic materials in the column bottom component (A_B) play a
10 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 into 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 of the present invention as a transesterification
15 reaction catalyst component.

In the present invention, it is particularly preferable to produce unsubstituted diphenyl carbonate or a lower hydrocarbon-substituted diphenyl carbonate by using unsubstituted phenol or a lower hydrocarbon-substituted phenol as the aromatic monohydroxy compound. In this case, the catalyst component and by-products
20 having a higher boiling point than that of the diphenyl carbonate such as phenyl salicylate, xanthone, a phenyl alkoxybenzoate and 1-phenoxy-carbonyl-2-phenoxy-carboxy-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
25 completely separated out 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
5 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
10 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, in general 90 to 97 % by weight of the liquid continuously fed in is continuously withdrawn from the top of the
15 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
20 weight of the alkyl aryl carbonate, 0.05 to 1 % by weight of intermediate boiling point by-products, and 52 to 84 % by weight of the diaryl carbonate; 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.

As stated above, the amount of the column top component (A_T) continuously
25 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 an inlet provided at a middle 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 from 1 to 9%, preferably from 3 to 8%, of the diaryl carbonate fed in.

The column bottom component (B_B) from the diaryl carbonate purifying column 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 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 from 0.05 to 0.5% of the diaryl carbonate fed in.

A high-purity diaryl carbonate is continuously withdrawn from the side cut outlet of the diaryl carbonate purifying column B, the amount thereof generally corresponding to approximately 90 to 98% 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 99.99%, more preferably not less than 99.999%. The content of the intermediate boiling point by-products having a boiling point between that of the alkyl

aryl carbonate and that of the diaryl carbonate is not more than 100 ppm, preferably not more than 30 ppm, more preferably not more than 10 ppm, or it may even be possible to make the side cut component (B_S) substantially not contain such intermediate boiling point by-products at all. Moreover, the content of the high boiling point by-products having a higher boiling point than that of the diaryl carbonate is not more than 100 ppm, preferably not more than 50 ppm, more preferably not more than 10 ppm.

The contents of high boiling point impurities in the diaryl carbonate obtained 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 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 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.

Moreover, in the present invention, a starting material and catalyst which do not contain 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 preferably not more than 1 ppb.

The column top component (B_T) continuously withdrawn from the top of the

diaryl carbonate purifying column B is continuously fed into the intermediate boiling point material separating column C from an inlet provided at a middle portion of the separating column C, and is continuously separated into three components, i.e. a column top component (C_T), a side cut component (C_S), and a column bottom component (C_B). The composition of the column top component (B_T) from the diaryl carbonate purifying column B is generally 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, 60 to 95 % by weight of the alkyl aryl carbonate, 0.05 to 2 % by weight of intermediate boiling point by-products, and 0.1 to 15 % by weight of the diaryl carbonate; the content of high boiling point by-products is generally not more than 500 ppm, preferably not more than 300 ppm.

The amount of the column top component (C_T) from the intermediate boiling point material separating column C is generally 80 to 97 % by weight of the column top component (B_T) fed in. The composition of the column top component (C_T) is generally 0.1 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, 60 to 95 % by weight of the alkyl aryl carbonate, and 0.05 to 0.5 % by weight of intermediate boiling point by-products; the content of the diaryl carbonate and high boiling point by-products is generally not more than 100 ppm, preferably not more than 10 ppm.

The amount of the side cut component (C_S) from the intermediate boiling point material separating column C is generally 1 to 10 % by weight of the column top component (B_T) fed in. The composition of the side cut component (C_S) is generally 0.01 to 5 % by weight of the aromatic monohydroxy compound, not more than 10 ppm of an alkyl aryl ether, 10 to 50 % by weight of the alkyl aryl carbonate, 10 to 70 % by weight of intermediate boiling point by-products, 5 to 60 % by weight

of the diaryl carbonate, and not more than 1 % by weight of high boiling point by-products.

The amount of the column bottom component (C_B) from the intermediate boiling point material separating column C is generally 3 to 15 % by weight of the column top component (B_T) fed in. The composition of the column bottom component (C_B) is generally 0.01 to 0.5 % by weight of the aromatic monohydroxy compound, not more than 10 ppm of an alkyl aryl ether, 0 to 3 % by weight of the alkyl aryl carbonate, 0 to 0.1 % by weight of intermediate boiling point by-products, 95 to 99.9 % by weight of the diaryl carbonate, and not more than 1 % by weight of high boiling point by-products.

It is preferable for some or all the column top component (C_T) separated off by the intermediate boiling point material separating column C as described above to be taken as starting material for the initial transesterification reaction and/or the reactive distillation of the present invention. The column top component (C_T) has low contents of the intermediate boiling point by-products and high boiling point by-products, and has a high content of the alkyl aryl carbonate, and hence in the present invention, it is particularly preferable to continuously feed the column top component (C_T) into the reactive distillation column in which the disproportionation reaction mainly occurs. Such reuse by recycling is particularly important in the case of industrial implementation.

Moreover, it is also preferable to recycle and thus reuse some or all of the column bottom component (C_B) separated off as described above. The column bottom component (C_B) has low contents of the intermediate boiling point by-products and high boiling point by-products, and has a high content of the diaryl carbonate, and hence is preferably recovered. Although the column bottom component (C_B) can also be continuously fed into the diaryl carbonate purifying

column B, it is particularly preferable to continuously feed the column bottom component (C_B) into the high boiling point material separating column A, since then the high-purity diaryl carbonate can be obtained with yet higher productivity. Such reuse by recycling is particularly important in the case of industrial implementation.

5 The term "prolonged stable operation" used in the present invention means that operation can be carried out continuously in a steady state based on the operating conditions with no reaction abnormalities, distillation abnormalities such as flooding, clogging of piping, or erosion for not less than 1000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours, and a
10 predetermined amount of the high-purity diaryl carbonate can be produced while maintaining high selectivity.

 In the case of 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, the content of intermediate boiling
15 point by-products contained in the unsubstituted or lower hydrocarbon-substituted diphenyl carbonate obtained is not more than 100 ppm, preferably not more than 30 ppm, more preferably not more than 10 ppm, yet more preferably not more than 1 ppm, and the contents of high boiling point impurities are not more than 30 ppm, preferably not more than 10 ppm, more preferably not more than 1 ppm for phenyl
20 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
25 hydrocarbon-substituted derivative thereof, and not more than 30 ppm, preferably not more than 10 ppm, more preferably not more than 5 ppm for
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.

Moreover, in the present invention, a dialkyl carbonate, phenol or lower
5 hydrocarbon-substituted phenol, and catalyst each not containing a halogen are generally used, and hence the halogen content of the unsubstituted or lower hydrocarbon-substituted diphenyl carbonate obtained is not more than 0.1 ppm, preferably not more than 10 ppb, more preferably not more than 1 ppb.

The diaryl carbonate obtained in the present invention is of very high purity,
10 and hence is particularly preferably used as a raw material for the production of an aromatic polycarbonate through transesterification with an aromatic dihydroxy compound.

Furthermore, an aromatic polycarbonate using as a raw material thereof a high-purity diphenyl carbonate obtained through the present invention is uncolored
15 and of high purity and high performance, and hence can be preferably used as an optical disk which is a recording medium for information, music, images and so on, or as any of various engineering plastics. A process for the production of an aromatic polycarbonate through transesterification between the high-purity diphenyl carbonate of the present invention and an aromatic dihydroxy compound may be any process,
20 but a particularly preferable process that makes good use of the properties of the high-purity diphenyl carbonate of the present invention is a process proposed by the present inventors in which polymerization is carried out while making a molten prepolymer drop down along a guide fixed in space (see, for example, WO 99/64492).

25 The material constituting the reactive distillation column, the high boiling point material separating column A, the diaryl carbonate purifying column B, the

intermediate boiling point material separating column C, and other liquid-contacting parts used 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.

5

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
10 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>

15 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 an internal, two sets of Mellapak (total number of stages 11) were installed in the upper portion, and sieve trays each having the cross-sectional area per hole of approximately 1.3 cm^2 and a number of holes of approximately $250 / \text{m}^2$
20 were used in the lower portion.

<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.

25 <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.

<Intermediate boiling point material separating column C>

A continuous multi-stage distillation column as shown in FIG. 2 having $L_C =$
5 1500 cm and $D_C = 150$ cm, and having three sets of Mellapak with $n_4 = 6$, $n_5 = 10$, and $n_6 = 7$ installed therein as the internal was used as the intermediate boiling point material separating column C.

<Reactive distillation>

A reaction mixture containing 18.7 % by weight of methyl phenyl carbonate
10 that had been obtained by subjecting phenol and dimethyl carbonate containing anisole to a transesterification reaction was used as a starting material. This starting material contained 27.5 % by weight of dimethyl carbonate, 8.2 % by weight of anisole, 43.9 % by weight of phenol, 1.5 % by weight of diphenyl carbonate, 0.1 % by weight of intermediate boiling point by-products, and 110 ppm of high boiling point
15 by-products, and further contained approximately 100 ppm of $Pb(OPh)_2$ as a catalyst. The starting material substantially did not contain halogens (lower than 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. 2 at a flow rate of 83.33 ton / hr from a starting material inlet 101 installed
20 between the Mellapak and the sieve trays. Reactive distillation was carried out continuously under conditions of a temperature at the bottom of the column of 210°C, a pressure at the top of the column of 3×10^4 Pa, and a reflux ratio of 0.3.

<Separation, purification, and reuse by recycling>

A high boiling point reaction mixture containing diphenyl carbonate was
25 continuously withdrawn from the bottom of the reactive distillation column, and was continuously fed into a lower portion of the high boiling point material separating

column A from an inlet A1. Separation by distillation was carried out continuously under conditions of a column bottom temperature in the high boiling point material separating column A of 205°C, a column top pressure of 1900 Pa, and a reflux ratio of 0.6. A column top component (A_T) continuously withdrawn from the top of the

5 high boiling point material separating column A was continuously fed into the diaryl carbonate purifying column B from an inlet B1. Separation by distillation was carried out continuously under conditions of a column bottom temperature in the diaryl carbonate purifying column B of 208°C, a column top pressure of 5000 Pa, and a reflux ratio of 2.0. Diphenyl carbonate was continuously withdrawn from a side

10 cut outlet B2 of the purifying column B.

A column top component (B_T) continuously withdrawn from the top of the diaryl carbonate purifying column B was continuously fed into the intermediate boiling point material separating column C from an inlet C1. Separation by distillation was carried out continuously under conditions of a column bottom

15 temperature in the intermediate boiling point material separating column C of 170°C, a column top pressure of 4800 Pa, and a reflux ratio of 0.5. Intermediate boiling point material having intermediate boiling point by-products as a main component thereof was continuously withdrawn from a side cut outlet C2 of the intermediate boiling point material separating column C. A column top component (C_T)

20 continuously withdrawn from the top of the intermediate boiling point material separating column C was recycled and thus reused by being continuously fed into the reactive distillation column. A column bottom component (C_B) continuously withdrawn from the bottom of the intermediate boiling point material separating column C was recycled and thus reused by being continuously fed as is into the

25 lower portion of the high boiling point material separating column A.

When all of the distillation columns had reached to a stable steady state, the

flow rate for the starting material fed into the reactive distillation column was 83.33 ton / hr for the fresh starting material and 3.33 ton / hr for the column top component (C_T) from the intermediate boiling point material separating column C that was recycled and thus reused, i.e. 86.66 ton / hr in total. The flow rate for the high boiling point reaction mixture continuously withdrawn from the bottom of the reactive distillation column was 10.00 ton / hr, and the composition thereof was 0.1 % by weight of dimethyl carbonate, 0.05 % by weight of anisole, 1.2 % by weight of phenol, 29.5 % by weight of methyl phenyl carbonate, 68.0 % by weight of diphenyl carbonate, 0.25 % by weight of intermediate boiling point by-products, and 0.9 % by weight of high boiling point by-products including the catalyst.

The flow rate for the material fed into the high boiling point material separating column A was 10.00 ton / hr for the above high boiling point reaction mixture and 1.11 ton / hr for the column bottom component (C_B) from the intermediate boiling point material separating column C that was recycled and thus reused, i.e. 11.11 ton / hr in total. The flow rate for the column top component (A_T) continuously withdrawn from the top of the high boiling point material separating column A was 10.56 ton / hr. The flow rate for the column top component (B_T) continuously withdrawn from the diaryl carbonate purifying column B was 4.50 ton / hr, the flow rate for the column bottom component (B_B) was 0.22 ton / hr, and the flow rate for the side cut component (B_S) was 5.84 ton / hr. The flow rate for the column top component (C_T) continuously withdrawn from the intermediate boiling point material separating column C was 3.33 ton / hr, the flow rate for the column bottom component (C_B) was 1.11 ton / hr, and the flow rate for the side cut component (C_S) was 0.06 ton / hr.

The composition of the side cut component (C_S) from the intermediate boiling point material separating column C was 0.7 % by weight of phenol, 24.3 % by weight

of methyl phenyl carbonate, a total of 37.6 % by weight of intermediate boiling point by-products (34.2 % by weight of methyl methoxybenzoate, 3.2 % by weight of 2-methoxyethyl-phenyl carbonate, and 0.2 % by weight of cresyl phenyl ether), 38.8 % by weight of diphenyl carbonate, and 0.3 % by weight of high boiling point by-products, and hence the intermediate boiling point by-products were concentrated therein. The column top component (C_T) from the intermediate boiling point material separating column C contained 8.5 % by weight of phenol, and 90.5 % by weight of methyl phenyl carbonate. The column bottom component (C_B) from the intermediate boiling point material separating column C contained 1.8 % by weight of methyl phenyl carbonate, and 97.2 % by weight of diphenyl carbonate.

The content of diphenyl carbonate in the side cut component (B_S) from the diaryl carbonate purifying column B was at least 99.999 % by weight, and each of intermediate boiling point by-products and high boiling point by-products were undetectable, the content thereof being not more than 1 ppm. Moreover, the halogen content of the diphenyl carbonate was undetectable, the content thereof being not more than 1 ppb.

It was possible to continuously carry out the above reactive distillation and separation / purification by distillation stably for 5000 hours; the analytical values after 500 hours, 1000 hours, 3000 hours, and 5000 hours were each approximately the same as above, and hence it was possible to stably obtain high-purity diphenyl carbonate substantially not containing intermediate boiling point by-products and high boiling point by-products.

Comparative Example 1:

Reactive distillation and separation / purification by distillation were carried out using the same process as in Example 1, except that the intermediate boiling

point material separating column C was not used, but rather the column top component (B_T) from the diaryl carbonate purifying column B was reused by recycling into the reactive distillation column. Up to the elapse of 50 hours, diphenyl carbonate was obtained with approximately the same results as in Example 1, but
5 the content of intermediate boiling point by-products such as methyl methoxybenzoate and 2-methoxyethyl-phenyl carbonate then increased continuously, being 10 ppm after 100 hours, 25 ppm after 200 hours, and 40 ppm after 300 hours.

Example 2:

10 Reactive distillation and separation / purification by distillation were carried out using the same process as in Example 1, except that the conditions for the separation / purification by distillation were changed to a column bottom temperature of 210°C, a column top pressure of 3800 Pa, and a reflux ratio of 0.61 for the high boiling point material separating column A, a column bottom temperature of 220°C, a
15 column top pressure of 6700 Pa, and a reflux ratio of 1.5 for the diaryl carbonate purifying column B, and a column bottom temperature of 200°C, a column top pressure of 2400 Pa, and a reflux ratio of 0.35 for the intermediate boiling point material separating column C. The purity of the diphenyl carbonate after 500 hours and 1000 hours was at least 99.999 % by weight, and each of intermediate boiling
20 point by-products and high boiling point by-products were undetectable, the content thereof being not more than 1 ppm. Moreover, the halogen content of the diphenyl carbonate was undetectable, the content thereof being not more than 1 ppb.

Example 3:

25 Using the diphenyl carbonate obtained in Example 1, an aromatic polycarbonate was produced using the process described in example 1 in

International Publication No. 99/64492. The obtained aromatic polycarbonate having the number average molecular weight of 10500 was injection molded at 310°C into a test piece (3.2mm thickness). This test piece had b* value of 3.2 (this value indicating a yellowness in accordance with a CIELAB method) and no yellow
5 tinge, and was uncolored, which was excellent in transparency. After crushing these test pieces by a crushing machine, injection molding of the crushed pieces at 310°C was repeated five times, whereupon the b* value of the test piece thus obtained was 3.5, and hence marked discoloration was not observed. Moreover, a heat resistance ageing test (120°C, 500 hours) was carried out on the test piece (b*
10 value = 3.2) produced by injection molding the above aromatic polycarbonate, whereupon the b* value was 3.5, and hence marked discoloration was not observed.

For the test piece of an aromatic polycarbonate obtained by the same process using diphenyl carbonate containing 150 ppm of each of intermediate boiling point by-products and high boiling point by-products and having a chlorine content of
15 0.2 ppm, the b* value was 3.6. As described above, the b* value of the molding piece after repeatedly injection molding at 310°C five times was 4.2, and the b* value after the heat resistance ageing test (120°C, 500 hours) was 4.0. The test pieces in the above two cases exhibited light yellow.

20 Industrial Applicability

The present invention can be suitably used as a 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 prolonged period of time of not less than 2000 hours on an industrial scale of not less than 1 ton / hr from a
25 reaction mixture containing an alkyl aryl carbonate obtained through a transesterification reaction between a dialkyl carbonate and an aromatic

monohydroxy compound.

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 that 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 said 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, wherein the improvement comprises:

at least three continuous multi-stage distillation columns comprising:

(a) a high boiling point material separating column A comprising 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 (1) to (3);

$$800 \leq L_A \leq 3000 \quad (1)$$

$$100 \leq D_A \leq 1000 \quad (2)$$

$$20 \leq n_A \leq 100 \quad (3),$$

(b) a diaryl carbonate purifying column B comprising a continuous multi-stage distillation column having a side cut outlet, a length L_B (cm), an inside diameter D_B (cm), and an internal with a number of stages n_B thereinside, wherein L_B , D_B , and n_B satisfy the following formulae (4) to (6);

$$1000 \leq L_B \leq 5000 \quad (4)$$

$$100 \leq D_B \leq 1000 \quad (5)$$

$$20 \leq n_B \leq 70 \quad (6), \text{ and}$$

(c) an intermediate boiling point material separating column C comprising a
 5 continuous multi-stage distillation column having a side cut outlet, a length L_C (cm),
 an inside diameter D_C (cm), and an internal with a number of stages n_C therein, inside,
 wherein L_C , D_C , and n_C satisfy the following formulae (7) to (9);

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

$$50 \leq D_C \leq 500 \quad (8)$$

$$10 \leq n_C \leq 50 \quad (9),$$

wherein said three continuous multi-stage distillation columns are arranged
 in this order.

2. The process according to claim 1, wherein not less than 1 ton / hr of the
 15 high-purity diaryl carbonate is obtained continuously as a side cut component B_S
 from said diaryl carbonate purifying column B.

3. The process according to claim 1 or 2, wherein said high boiling point
 reaction mixture containing the diaryl carbonate continuously withdrawn from the
 20 lower portion of said reactive distillation column in a liquid form is:

(a) continuously introduced into said high boiling point material separating
 column A, and continuously subjected to 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 a high boiling point material,

25 (b) said column top component A_T is continuously introduced into said diaryl
 carbonate purifying column B, and continuously subjected to separation by distillation

into a column top component B_T , the side cut component B_S , and a column bottom component B_B , and

(c) said column top component B_T is continuously introduced into said intermediate boiling point material separating column C, and continuously subjected to separation by distillation into a column top component C_T containing the alkyl aryl carbonate, a side cut component C_S containing an intermediate boiling point material having a boiling point between that of the alkyl aryl carbonate and that of the diaryl carbonate, and a column bottom component C_B containing the diaryl carbonate.

4. The process according to any one of claims 1 to 3, wherein the column top component C_T from said intermediate boiling point material separating column C is continuously fed into said reactive distillation column.

5. The process according to any one of claims 1 to 4, wherein the column bottom component C_B from said intermediate boiling point material separating column C is continuously fed into said high boiling point material separating column A.

6. The process according to any one of claims 1 to 5, wherein said reactive distillation column comprises a continuous multi-stage distillation column having a length L (cm), an inside diameter D (cm), and an internal with a number of stages n therein, and having 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 (10) to (15):

$$1500 \leq L \leq 8000 \quad (10)$$

$$100 \leq D \leq 2000 \quad (11)$$

$$5 \quad 2 \leq L/D \leq 40 \quad (12)$$

$$10 \leq n \leq 80 \quad (13)$$

$$2 \leq D/d_1 \leq 15 \quad (14)$$

$$5 \leq D/d_2 \leq 30 \quad (15).$$

10 7. The process according to any one of claims 1 to 6, wherein said diaryl carbonate purifying column B comprises a continuous multi-stage distillation column having an inlet B1 at a middle portion of the column, a side cut outlet B2 between said inlet B1 and the column bottom, and having a number of stages n_1 of an internal above the inlet B1, a number of stages n_2 of an internal between the inlet B1 and the
15 side cut outlet B2, and a number of stages n_3 of an internal below the side cut outlet B2, the total number of stages ($n_1 + n_2 + n_3$) being n_B , wherein n_1 , n_2 , and n_3 satisfy the following formulae (16) to (18):

$$5 \leq n_1 \leq 20 \quad (16)$$

$$12 \leq n_2 \leq 40 \quad (17)$$

$$20 \quad 3 \leq n_3 \leq 15 \quad (18).$$

8. The process according to any one of claims 1 to 7, wherein said intermediate boiling point material separating column C comprises a continuous multi-stage distillation column having an inlet C1 at a middle portion of the column, a
25 side cut outlet C2 between said inlet C1 and the column bottom, and having a number of stages n_4 of an internal above the inlet C1, a number of stages n_5 of an

internal between the inlet C1 and the side cut outlet C2, and a number of stages n_6 of an internal below the side cut outlet C2, the total number of stages ($n_4 + n_5 + n_6$) being n_c , wherein n_4 , n_5 , and n_6 satisfy the following formulae (19) to (21):

$$2 \leq n_4 \leq 15 \quad (19)$$

$$5 \leq n_5 \leq 30 \quad (20)$$

$$3 \leq n_6 \leq 20 \quad (21).$$

9. The process according to any one of claims 1 to 8, wherein each of said reactive distillation column, said high boiling point material separating column A, said diaryl carbonate purifying column B, and said intermediate boiling point material separating column C comprises a distillation column having a tray and/or a packing as the internal.

10. The process according to claim 9, wherein said reactive distillation column comprises 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, said diaryl carbonate purifying column B and said intermediate boiling point material separating column C is the packing.

20

11. The process according to claim 9 or 10, wherein said packing is a structured packing of at least one type selected from the group consisting of Mellapak, Gempak, TECHNO-PAK, Flexipac, a Sulzer packing, a Goodroll packing, and a Glitchgrid.

25

12. The process according to claim 9 or 10, wherein said tray in said

reactive distillation column is a sieve tray having a sieve portion and a down comer portion.

13. The process according to claim 12 wherein said sieve tray has 100 to
5 1000 holes / m² in the sieve portion.

14. The process according to claim 12 or 13, wherein the cross-sectional
area per hole of said sieve tray is in a range of from 0.5 to 5 cm².

10 15. The process according to any one of claims 1 to 14, wherein 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 a column top
pressure P_A in a range of from 1000 to 20000 Pa.

15 16. The process according to any one of claims 1 to 15, wherein 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 a column top pressure
P_B in a range of from 1000 to 20000 Pa.

20 17. The process according to any one of claims 1 to 16, wherein distillation
operation of said intermediate boiling point material separating column C is carried
out at a column bottom temperature T_C in a range of from 150 to 280°C, and a
column top pressure P_C in a range of from 500 to 18000 Pa.

25 18. The process according to any one of claims 1 to 17, wherein a reflux
ratio for said high boiling point material separating column A is in a range of from

0.01 to 10.

19. The process according to any one of claims 1 to 18, wherein a reflux ratio for said diaryl carbonate purifying column B is in a range of from 0.01 to 10.

5

20. The process according to any one of claims 1 to 19, wherein a reflux ratio for said intermediate boiling point material separating column C is in a range of from 0.01 to 10.

10 21. A high-purity diphenyl carbonate that is a diaryl carbonate produced by the process according to any one of claims 1 to 20, the diphenyl carbonate being unsubstituted or substituted with a lower hydrocarbon, and having a halogen content of not more than 0.1 ppm, a content of said intermediate boiling point material of not more than 100 ppm, and a content of by-products having a higher boiling point than
15 that of the diphenyl carbonate of not more than 100 ppm.

22. The high-purity diphenyl carbonate according to claim 21, wherein the diphenyl carbonate is unsubstituted diphenyl carbonate, and the halogen content is not more than 10 ppb, the content of said intermediate boiling point material is not
20 more than 30 ppm, 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 a higher boiling point than that of the diphenyl carbonate, is not more than 30 ppm.

25 23. The high-purity diphenyl carbonate according to claim 22, wherein the content of said intermediate boiling point material is not more than 10 ppm, and the

content of the by-products having a higher boiling point than that of the diphenyl carbonate is not more than 50 ppm.

24. The high-purity diphenyl carbonate according to claim 23, wherein the
5 halogen content is not more than 1 ppb, and the content of the by-products having a higher boiling point than that of the diphenyl carbonate is not more than 10 ppm.

25. A process for the production of an aromatic polycarbonate, comprising
using the high-purity diphenyl carbonate according to any one of claims 21 to 24 as a
10 raw material for the production of an aromatic polycarbonate through transesterification with an aromatic dihydroxy compound.

26. An aromatic polycarbonate produced by the process according to claim
25.

15 27. An apparatus for producing 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 that has been obtained through a transesterification reaction between a dialkyl carbonate and an aromatic
20 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 said column, continuously withdrawing a low boiling point reaction mixture containing a produced dialkyl carbonate from an upper portion
25 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, the apparatus comprising:

(a) a high boiling point material separating column A comprising 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

5 the following formulae (1) to (3);

$$800 \leq L_A \leq 3000 \quad (1)$$

$$100 \leq D_A \leq 1000 \quad (2)$$

$$20 \leq n_A \leq 100 \quad (3),$$

(b) a diaryl carbonate purifying column B which is connected said high boiling
10 point material separating column A, and which comprises a continuous multi-stage distillation column having a side cut outlet, a length L_B (cm), an inside diameter D_B (cm), and an internal with a number of stages n_B therein, wherein L_B , D_B , and n_B satisfy the following formulae (4) to (6);

$$1000 \leq L_B \leq 5000 \quad (4)$$

$$15 \quad 100 \leq D_B \leq 1000 \quad (5)$$

$$20 \leq n_B \leq 70 \quad (6), \text{ and}$$

(c) an intermediate boiling point material separating column C which is connected to said diaryl carbonate purifying column B, and which comprises a continuous multi-stage distillation column having a side cut outlet, a length L_C (cm),
20 an inside diameter D_C (cm), and an internal with a number of stages n_C therein, wherein L_C , D_C , and n_C satisfy the following formulae (7) to (9);

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

$$50 \leq D_C \leq 500 \quad (8)$$

$$10 \leq n_C \leq 50 \quad (9).$$

25

28. The apparatus according to claim 27, wherein said reactive distillation

column comprises a continuous multi-stage distillation column having a length L (cm), an inside diameter D (cm), and an internal with a number of stages n therein, and having 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 (10) to (15):

$$1500 \leq L \leq 8000 \quad (10)$$

$$100 \leq D \leq 2000 \quad (11)$$

$$2 \leq L / D \leq 40 \quad (12)$$

$$10 \leq n \leq 80 \quad (13)$$

$$2 \leq D / d_1 \leq 15 \quad (14)$$

$$5 \leq D / d_2 \leq 30 \quad (15).$$

29. The apparatus according to claim 27 or 28, wherein said diaryl carbonate purifying column B comprises a continuous multi-stage distillation column having an inlet B1 at a middle portion of the column, a side cut outlet B2 between said inlet B1 and the column bottom, and having a number of stages n_1 of an internal above the inlet B1, a number of stages n_2 of an internal between the inlet B1 and the side cut outlet B2, and a number of stages n_3 of an internal below the side cut outlet B2, the total number of stages ($n_1 + n_2 + n_3$) being n_B , wherein n_1 , n_2 , and n_3 satisfy the following formulae (16) to (18):

$$5 \leq n_1 \leq 20 \quad (16)$$

$$12 \leq n_2 \leq 40 \quad (17)$$

$$3 \leq n_3 \leq 15 \quad (18).$$

30. The apparatus according to any one of claims 27 to 29, wherein said intermediate boiling point material separating column C comprises a continuous multi-stage distillation column having an inlet C1 at a middle portion of the column, a side cut outlet C2 between said inlet C1 and the column bottom, and having a number of stages n_4 of an internal above the inlet C1, a number of stages n_5 of an internal between the inlet C1 and the side cut outlet C2, and a number of stages n_6 of an internal below the side cut outlet C2, the total number of stages ($n_4 + n_5 + n_6$) being n_C , wherein n_4 , n_5 , and n_6 satisfy the following formulae (19) to (21):

$$2 \leq n_4 \leq 15 \quad (19)$$

$$5 \leq n_5 \leq 30 \quad (20)$$

$$3 \leq n_6 \leq 20 \quad (21).$$