

PROCESS FOR INDUSTRIALLY PRODUCING HIGH-QUALITY AROMATIC POLYCARBONATE

Technical Field

The present invention relates to an industrial process for the production of an aromatic polycarbonate. More particularly, the present invention relates to a process for industrially producing large amounts of a high-quality and a high-performance aromatic polycarbonate having excellent mechanical properties and no coloration stably for a prolonged period of time from a dialkyl carbonate and an aromatic dihydroxy compound.

Background Art

Aromatic polycarbonates are widely used in many fields as engineering plastics having excellent heat resistance, impact resistance, transparency and so on. A variety of studies have been carried out hitherto into processes for producing such aromatic carbonates, and of these, an interfacial condensation polymerization process between phosgene and aromatic dihydroxy compounds such as 2,2-bis(4-hydroxyphenyl)propane (hereinafter referred to as "bisphenol A") has been industrialized. However, there are many problems with this interfacial condensation polymerization process, for example toxic phosgene must be used, methylene chloride, which has health and environmental problems, must be used as a polymerization solvent in a large amount of at least 10 times that of the polycarbonate, the apparatus is corroded by chlorine-containing compounds such as

methylene chloride and by-produced hydrogen chloride and sodium chloride, separating out residual chlorinated impurities such as sodium chloride and methylene chloride that have an adverse effect on the polymer properties is difficult, and treatment of a large amount of process wastewater containing methylene chloride, unreacted bisphenol A and so on is necessary.

On the other hand, as a process for producing the aromatic polycarbonates from the aromatic dihydroxy compounds and the diphenyl carbonate, a melt process in which, for example, bisphenol A and diphenyl carbonate are subjected to transesterification in a molten state, and polymerization is carried out while removing by-produced phenol has been known from hitherto. This transesterification reaction is an equilibrium reaction, and moreover the equilibrium constant is low, and hence the polymerization will not proceed unless the phenol is removed efficiently from the surface of the molten matter. Unlike the interfacial condensation polymerization process, the melt process has advantages such as a solvent not being used, but on the other hand there has been a problem intrinsic to the aromatic polycarbonates that once the polymerization has proceeded to a certain extent the viscosity of the polymer increases rapidly, and hence it becomes difficult to remove by-produced phenol and so on out of the polymerization system efficiently, whereby it becomes impossible to substantially increase the polymerization degree. That is, in the case of the aromatic polycarbonates, unlike in the case of molten condensation polymerization to produce another condensation polymer such as a polyamide or a polyester, the melt viscosity becomes extremely high even in a low

molecular weight state, for example at a polymerization degree (n) of 15 to 20, and hence surface renewal becomes very difficult using ordinary stirring. Removal of phenol from the polymer surface thus substantially stops occurring, and hence a polymer having a polymerization degree required for a product (n approximately 35 to 65) cannot be produced. This is well known in the person skilled in the art.

As polymerization apparatuses for producing the aromatic polycarbonates using such a melt process, various polymerization apparatuses are known. A process using a vertical stirring tank type polymerization apparatus having a stirrer is widely known. However, with such a vertical stirring tank type polymerization apparatus, in the case of small scale production, the volumetric efficiency is high, and there is the advantage of the apparatus being simple, and hence the polymerization can be made to proceed efficiently, but in the case of industrial scale production, it is difficult to efficiently remove from the system phenol that is by-produced as the polymerization proceeds as described above, and hence there is the problem that the polymerization rate is very low. Furthermore, for a large scale vertical stirring tank type polymerization apparatus, a ratio of the liquid volume to the evaporation area is generally greater than in the case of a small scale, the state being such that the so-called liquid depth is high. Consequently, even if the degree of vacuum is increased so as to increase the polymerization degree, because there is a high liquid depth in the lower portion of the stirring tank, the polymerization takes place at a higher pressure corresponding to the liquid depth than in the space in the upper portion of the stirring tank, and hence efficiently removing phenol or the like is

difficult. A large scale vertical stirring tank type polymerization apparatus can thus only be used in the case of producing a prepolymer. To attain the required polymerization degree, a polymerization apparatus for further subjecting this prepolymer to condensation polymerization is essential.

Various means have been used for efficiently removing phenol or the like from a high-viscosity polymer so as to solve the above problems. Most of these means have related to improving the mechanical stirring, for example, there have been described a process using a screw type polymerization apparatus having a vent (see Patent Document 1: Japanese Patent Publication No. 50-19600 (corresponding to Brit. Patent No. 1007302)), a process using an interlocking type twin screw extruder (see Patent Document 2: Japanese Patent Publication No. 52-36159), and a process using a thin film evaporation type reactor such as a screw evaporator or a centrifugal thin film evaporator (see Patent Document 3: Japanese Patent Publication No. 53-5718 (corresponding to U.S. Patent No. 3,888,826)), and furthermore there has been specifically disclosed a process using a combination of a centrifugal thin film evaporator and a horizontal biaxial stirring type polymerization apparatus (see Patent Document 4: Japanese Patent Application Laid-open No. 2-153923). These processes all have carrying out mechanical stirring as the basis of the art, and hence there are naturally limitations, and thus the above problems have not been solved. That is, there are limitations on mechanical stirring itself in terms of being able to handle ultra-high melt viscosity, and hence various problems relating to the ultra-high melt viscosity of the aromatic polycarbonates have remained unresolved.

With the above processes, it is attempted to resolve these problems by raising the temperature so as to lower the melt viscosity at least a little.

That is, in these processes, the molten prepolymer is subjected to polymerization at a high temperature of around 300 °C and under a high vacuum while trying to bring about surface renewal through mechanical stirring, but even at this temperature the melt viscosity is still very high, and hence the extent of surface renewal cannot be made high. There are thus limitations on the polymerization degree of polycarbonates that can be produced using these processes, it being difficult to produce a high molecular weight grade product. Furthermore, with these processes, discoloration or deterioration in properties of the polymer obtained is liable to occur due to the reaction being carried out at a high temperature of around 300 °C, and moreover such discoloration or deterioration in properties of the polymer is also liable to occur due to air or foreign material leaking in through a vacuum seal of the stirrer. There are thus still many problems to be solved in order to produce the high-quality polycarbonate stably for a prolonged period of time.

The present inventors have discovered that these problems can be completely solved by developing a process in which mechanical stirring is not carried out, but rather a guide-contacting downflow type polymerization apparatus is used in which the molten prepolymer is subjected to polymerization while being made to fall down under its own weight along guides such as wires, and have previously filed patent applications (see, for example, Patent Document 5: Japanese Patent Application Laid-open No. 8-225641, Patent Document 6: Japanese Patent Application Laid-open No. 8-225643, Patent Document 7:

Japanese Patent Application Laid-open No. 8-325373, Patent Document 8: WO 97-22650, Patent Document 9: Japanese Patent Application Laid-open No. 10-81741, Patent Document 10: Japanese Patent Application Laid-open No. 10-298279, Patent Document 11: WO 99/36457, Patent Document 12: WO 99/64492). However, with such processes, there has been no disclosure or suggestion of a specific industrial production process that enables not less than 1 ton / hr of the aromatic polycarbonates to be produced.

Furthermore, to produce the aromatic polycarbonates on an industrial scale through transesterification, a high-purity diphenyl carbonate must be procured in a large amount on an industrial scale. Aromatic dihydroxy compounds such as high-purity bisphenol A are mass-produced industrially, and can easily be procured, but a high-purity diphenyl carbonate cannot be procured in a large amount on an industrial scale. It is thus necessary to produce the high-purity diphenyl carbonate.

As a process for producing the diphenyl carbonate, a process of reacting a phenol 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 present in the diphenyl carbonate produced using this process, and hence the diphenyl carbonate cannot be used as a starting material for the production of an aromatic polycarbonate as is. The reason for this is that such chlorinated impurities markedly inhibit the polymerization reaction in the transesterification method for producing the aromatic polycarbonate

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 hardly proceeds at all. To make the diphenyl carbonate capable of being used as the starting material of a transesterification method aromatic polycarbonate, a troublesome multi-stage separation / purification process involving thorough washing with a dilute aqueous alkaline solution and hot water, oil / water separation, distillation and so on is thus required. Furthermore, the yield decreases due to hydrolysis loss and distillation loss during this separation / purification process. There are thus many problems in carrying out this process economically on the industrial scale.

On the other hand, a process for producing the aromatic carbonates through transesterification reactions between the dialkyl carbonate and the phenol 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 have been many difficulties in producing aromatic carbonates industrially in large amounts using such a process.

Several proposals have been made to improve on the above difficulties, but most of these have related to development of a catalyst to increase the reaction rate. Many metal compounds have been proposed as catalysts for this type of transesterification reaction. However, the problem of the disadvantageous equilibrium cannot be resolved merely by developing a catalyst, and hence there are very many issues to be

resolved including the reaction system in order to provide a process for industrial production aiming for mass production.

Attempts have also been made 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 method in which methanol produced as a by-product is distilled off by azeotropy together with an azeotrope-forming agent (see Patent Document 13: Japanese Patent Application Laid-Open No. 54-48732 (corresponding to West German Patent Application Laid-Open No. 736063, and U.S. Patent No. 4252737)), and a method in which the methanol produced as a by-product is removed by being adsorbed onto a molecular sieve (see Patent Document 14: Japanese Patent Application Laid-Open No. 58-185536 (corresponding to U.S. Patent No. 410464)). Moreover, a method has also been proposed in which, using an apparatus in which a distillation column is provided on top of a reactor, an alcohol produced as a by-product in the reaction is separated off from the reaction mixture, and at the same time unreacted starting material that evaporates is separated off by distillation (see Patent Document 15: Japanese Patent Application Laid-Open No. 56-123948 (corresponding to U.S. Patent No. 4182726)).

However, these reaction systems are basically batch system or switchover system. This is because there is a limitation on how much the reaction rate can be improved through catalyst development for such a transesterification reaction, and hence the reaction rate is still slow, and thus it has been thought that a 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 top of a reactor has been proposed as a continuous system, but there are problems such as the reaction rate being slow, and the gas-liquid interface in the reactor being small based on the volume of the liquid. It is thus not possible to make the conversion high. Accordingly, it is difficult to attain the object of producing the aromatic carbonates 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.

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 dialkyl carbonate and an aromatic hydroxy compound are continuously fed into a multi-stage distillation column, and reaction is carried out continuously inside the column in which a catalyst is present, while continuously withdrawing by distillation a low boiling point component containing an alcohol produced as a by-product, and continuously withdrawing a component containing a produced alkyl phenyl carbonate from a lower portion of the column (see Patent Document 16: Japanese Patent Application Laid-Open No. 3-291257), a reactive distillation method in which an alkyl phenyl carbonate is continuously fed into a multi-stage distillation column, and reaction is carried out continuously inside the

column in which a catalyst is present, while continuously withdrawing by distillation a low boiling point component containing a dialkyl carbonate produced as a by-product, and continuously withdrawing a component containing a produced diphenyl carbonate from a lower portion of the column (see Patent Document 17: 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 diphenyl carbonate is produced continuously while efficiently recycling a dialkyl carbonate produced as a by-product (see Patent Document 18: Japanese Patent Application Laid-Open No. 4-211038 (corresponding to WO 91/09832, European Patent No. 0461274, and U.S. Patent No. 5210268)), and a reactive distillation method in which a dialkyl carbonate and an aromatic hydroxy compound or the like are continuously fed into a multi-stage distillation column, and a liquid that flows down through the column is withdrawn from a side outlet provided at a middle 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 in 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 Document 19: Japanese Patent Application Laid-Open No. 4-235951).

These reactive distillation methods proposed by the present inventors are the first to enable the aromatic carbonates to be produced continuously and efficiently, and processes in which the diphenyl carbonate is produced from the dialkyl carbonate using two continuous

multi-stage distillation columns based on the above disclosures have been proposed thereafter (see, for example, Patent Document 20: Japanese Patent Application Laid-Open No. 6-157424 (corresponding to European Patent No. 0582931, and U.S. Patent No. 5334742), Patent Document 21: Japanese Patent Application Laid-Open No. 6-184058 (corresponding to European Patent No. 0582930, and U.S. Patent No. 5344954), Patent Document 22: Japanese Patent Application Laid-Open No. 9-40616, Patent Document 23: Japanese Patent Application Laid-Open No. 9-59225, Patent Document 24: Japanese Patent Application Laid-Open No. 9-176094, Patent Document 25: WO 00/18720 (corresponding to U.S. Patent No. 6093842), Patent Document 26: Japanese Patent Application Laid-Open No. 2001-64235).

Among 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 required, a method in which 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 27: WO 97/11049 (corresponding to European Patent No. 0855384, and U.S. Patent No. 5872275)), and a method carried out while keeping the weight ratio of a polyhydric aromatic hydroxy compound in the reaction system to a catalyst metal at not more than 2.0 (see Patent Document 28: 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 proposed a method in which 70 to 99 % by weight of phenol

produced as a by-product in a polymerization process is used as a starting material, and diphenyl carbonate is produced using a reactive distillation method; this diphenyl carbonate can be used as a starting material for polymerization to produce an aromatic polycarbonate (see Patent Document 29: Japanese Patent Application Laid-open No. 9-255772 (corresponding to European Patent No. 0892001, and U.S. Patent No. 5747609)).

However, in all of these prior art documents in which the production of aromatic carbonates using a 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. 1 ton / hr), nor is there any description suggesting such a process or apparatus. For example, the descriptions regarding heights (H_1 and H_2 : cm), diameters (D_1 and D_2 : cm), numbers of stages (n_1 and n_2), and starting material feeding rates (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 Table 1.

Table 1

TABLE 1

H ₁	D ₁	n ₁	Q ₁	H ₂	D ₂	n ₂	Q ₂	PATENT DOCUMENTS
600	25	20	66	600	25	20	23	18
350	2.8	-	0.2	305	5~10	15+ PACKINGS	0.6	21
500	5	50	0.6	400	8	50	0.6	22
100	4	-	1.4	200	4	-	0.8	23
300	5	40	1.5	-	5	25	0.7	24
1200	20	40	86	600	25	20	31	27 28
600	-	20	66	600	-	20	22	29

In other words, the biggest pairs of continuous multi-stage distillation columns used when carrying out this reaction using the reactive distillation system are those disclosed by the present applicants in Patent Document 27 (WO 97/11049 (corresponding to European Patent No. 0855384, and U.S. Patent No. 5872275)) and Patent Document 28 (Japanese Patent Application Laid-Open No. 11-92429 (corresponding to European Patent No. 1016648, and U.S. Patent No. 6262210)). As can be seen from Table 1, the maximum values of the various conditions for the continuous multi-stage distillation columns disclosed for the above reaction are H₁ = 1200 cm, H₂ = 600 cm, D₁ = 20 cm, D₂ = 25 cm, n₁ = n₂ = 50 (only this condition, Patent Document 22 (Japanese Patent Application Laid-Open No. H9-40616)), Q₁ = 86 kg / hr, and Q₂ = 31 kg / hr, and an produced amount of the diphenyl carbonate has not exceeded approximately 6.7 kg / hr, which is not an amount produced on an industrial scale.

Disclosure of the Invention

It is an object of the present invention to provide a specific process that enables a high-quality and high-performance aromatic polycarbonate having excellent mechanical properties and no discoloration to be produced industrially in a large amount (e.g. not less than 1 ton / hr) stably for a prolonged period of time (e.g. not less than 1000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours) from a dialkyl carbonate and an aromatic dihydroxy compound.

The present inventors have carried out studies aimed at discovering a specific process enabling the above object to be attained, and as a result have reached to the present invention. That is, according to the first aspect of the present invention, there are provides:

1. an industrial process for the production of a high-quality aromatic polycarbonate in which an aromatic polycarbonate is continuously produced from a dialkyl carbonate and an aromatic dihydroxy compound, the process comprising the steps of:

- (I) continuously producing a diphenyl carbonate by taking the dialkyl carbonate and a phenol as a starting material, continuously feeding the starting material into a first continuous multi-stage distillation column in which a homogeneous catalyst is present, carrying out reaction and distillation simultaneously in said first column, continuously withdrawing a first column low boiling point reaction mixture containing a produced alcohol from an upper portion of said first column in a gaseous form, continuously withdrawing a first column high boiling point reaction

mixture containing a produced alkyl phenyl carbonate from a lower portion of said first column in a liquid form, continuously feeding said first column high boiling point reaction mixture into a second continuous multi-stage distillation column in which a catalyst is present, carrying out reaction and distillation simultaneously in said second column, continuously withdrawing a second column low boiling point reaction mixture containing a produced dialkyl carbonate from an upper portion of said second column in a gaseous form, continuously withdrawing a second column high boiling point reaction mixture containing a produced diphenyl carbonate from a lower portion of said second column in a liquid form, and continuously feeding the second column low boiling point reaction mixture containing the dialkyl carbonate into the first continuous multi-stage distillation column;

(II) purifying the diphenyl carbonate by continuously introducing the second column high boiling point reaction mixture containing the diphenyl carbonate into a high boiling point material separating column A, and continuously carrying out separation by distillation into a column top component A_T containing the diphenyl carbonate and a column bottom component A_B containing the catalyst, and then continuously introducing said column top component A_T into a diphenyl carbonate purifying column B having a side cut outlet, and continuously carrying out separation by distillation into three components being a column top component B_T , a side cut component B_S and a column bottom component B_B , so as to obtain a high-purity diphenyl carbonate as the side cut component;

(III) producing the aromatic polycarbonate by reacting said aromatic dihydroxy compound and said high-purity diphenyl carbonate

together so as to produce an aromatic polycarbonate molten prepolymer, and said molten prepolymer being made to flow down along surfaces of guides by using a guide-contacting downflow type polymerization apparatus, so as to polymerize said molten prepolymer while flowing down; and

(IV) recycling a phenol by circulating phenol by-produced in step (III) back into the diphenyl carbonate production step (I);

wherein:

(a) said first continuous multi-stage distillation column comprises a structure having a cylindrical trunk portion having a length L_1 (cm) and an inside diameter D_1 (cm), and having an internal with number of stages n_1 thereinside, and comprises a gas outlet having an inside diameter d_{11} (cm) at a top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_{12} (cm) at a bottom of the column or in a lower portion of the column near to the bottom, at least one first inlet provided in the upper portion and / or a middle portion of the column below said gas outlet, and at least one second inlet provided in the middle portion and / or the lower portion of the column above said liquid outlet, wherein L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} respectively satisfy the following formulae (1) to (6);

$$1500 \leq L_1 \leq 8000 \quad (1),$$

$$100 \leq D_1 \leq 2000 \quad (2),$$

$$2 \leq L_1 / D_1 \leq 40 \quad (3),$$

$$20 \leq n_1 \leq 120 \quad (4),$$

$$5 \leq D_1 / d_{11} \leq 30 \quad (5), \text{ and}$$

$$3 \leq D_1 / d_{12} \leq 20 \quad (6);$$

(b) said second continuous multi-stage distillation column comprises a structure having a cylindrical trunk portion having a length L_2 (cm) and an inside diameter D_2 (cm), and having an internal with number of stages n_2 therein, and comprises a gas outlet having an inside diameter d_{21} (cm) at a top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_{22} (cm) at a bottom of the column or in a lower portion of the column near to the bottom, at least one third inlet provided in the upper portion and / or a middle portion of the column below said gas outlet, and at least one fourth inlet provided in the middle portion and / or the lower portion of the column above said liquid outlet, wherein L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} , and D_2 / d_{22} respectively satisfy the following formulae (7) to (12);

$$1500 \leq L_2 \leq 8000 \quad (7),$$

$$100 \leq D_2 \leq 2000 \quad (8),$$

$$2 \leq L_2 / D_2 \leq 40 \quad (9),$$

$$10 \leq n_2 \leq 80 \quad (10),$$

$$2 \leq D_2 / d_{21} \leq 15 \quad (11), \text{ and}$$

$$5 \leq D_2 / d_{22} \leq 30 \quad (12);$$

(c) said high boiling point material separating column A is a continuous multi-stage distillation column having a length L_A (cm) and an inside diameter D_A (cm), and having an internal with number of stages n_A therein, wherein L_A , D_A , and n_A satisfy the following formulae (13) to (15);

$$800 \leq L_A \leq 3000 \quad (13),$$

$$100 \leq D_A \leq 1000 \quad (14), \text{ and}$$

$$20 \leq n_A \leq 100 \quad (15),$$

and said diphenyl carbonate purifying column B is a continuous multi-stage distillation column having a length L_B (cm) and an inside diameter D_B (cm), having an internal thereinside, having an inlet B1 at a middle stage of the column, and a side cut outlet B2 between said inlet B1 and the column bottom, and having number of stages n_{B1} of the internal above the inlet B1, number of stages n_{B2} of the internal between the inlet B1 and the side cut outlet B2, number of stages n_{B3} of the internal below the side cut outlet B2, and a total number of stages $n_B (= n_{B1} + n_{B2} + n_{B3})$, wherein L_B , D_B , n_{B1} , n_{B2} , n_{B3} , and n_B satisfy the following formulae (16) to (21);

$$1000 \leq L_B \leq 5000 \quad (16),$$

$$100 \leq D_B \leq 1000 \quad (17),$$

$$5 \leq n_{B1} \leq 20 \quad (18),$$

$$12 \leq n_{B2} \leq 40 \quad (19),$$

$$3 \leq n_{B3} \leq 15 \quad (20), \text{ and}$$

$$20 \leq n_B \leq 70 \quad (21);$$

(d) said guide-contacting downflow type polymerization apparatus comprises:

(1) an apparatus having a molten prepolymer receiving port, a perforated plate, a polymerization reaction zone having a plurality of guides that extend downward from the perforated plate provided in a space surrounded by the perforated plate, a side casing and a tapered bottom casing, a molten prepolymer feeding zone for feeding the molten prepolymer via the perforated plate onto the guides in the polymerization reaction zone, a vacuum vent provided in the polymerization reaction zone, an aromatic polycarbonate discharge port provided in a lowermost

portion of the tapered bottom casing, and an aromatic polycarbonate discharge pump connected to the discharge port, wherein:

(2) an internal sectional area A (m^2) taken through a horizontal plane of the side casing in the polymerization reaction zone satisfies the formula (22),

$$0.7 \leq A \leq 300 \quad (22),$$

(3) a ratio between A (m^2) and an internal sectional area B (m^2) taken through a horizontal plane of the aromatic polycarbonate discharge port satisfies the formula (23),

$$20 \leq A / B \leq 1000 \quad (23),$$

(4) the tapered bottom casing in the polymerization reaction zone is connected at an internal angle C ($^\circ$) to the side casing thereabove, wherein the angle C ($^\circ$) satisfies the formula (24),

$$120 \leq C \leq 165 \quad (24),$$

(5) a length h (cm) of each guide satisfies the formula (25),

$$150 \leq h \leq 5000 \quad (25), \text{ and}$$

(6) a total external surface area S (m^2) of said guide satisfies the formula (26),

$$2 \leq S \leq 50000 \quad (26),$$

2. the process according to item 1, wherein not less than 1 ton / hr of the aromatic polycarbonate is produced,

3. the process according to item 1 or 2, wherein said d_{11} and said d_{12} satisfy the formula (27), and said d_{21} and said d_{22} satisfy the formula (28);

$$1 \leq d_{12} / d_{11} \leq 5 \quad (27); \text{ and}$$

$$1 \leq d_{21} / d_{22} \leq 6 \quad (28),$$

4. the process according to any one of items 1 to 3, wherein L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} for said first continuous multi-stage distillation column satisfy respectively $2000 \leq L_1 \leq 6000$, $150 \leq D_1 \leq 1000$, $3 \leq L_1 / D_1 \leq 30$, $30 \leq n_1 \leq 100$, $8 \leq D_1 / d_{11} \leq 25$, and $5 \leq D_1 / d_{12} \leq 18$, and L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} , and D_2 / d_{22} for said second continuous multi-stage distillation column satisfy respectively $2000 \leq L_2 \leq 6000$, $150 \leq D_2 \leq 1000$, $3 \leq L_2 / D_2 \leq 30$, $15 \leq n_2 \leq 60$, $2.5 \leq D_2 / d_{21} \leq 12$, and $7 \leq D_2 / d_{22} \leq 25$,
5. the process according to any one of items 1 to 4, wherein L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} for said first continuous multi-stage distillation column satisfy respectively $2500 \leq L_1 \leq 5000$, $200 \leq D_1 \leq 800$, $5 \leq L_1 / D_1 \leq 15$, $40 \leq n_1 \leq 90$, $10 \leq D_1 / d_{11} \leq 25$, and $7 \leq D_1 / d_{12} \leq 15$, and L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} , and D_2 / d_{22} for said second continuous multi-stage distillation column satisfy respectively $2500 \leq L_2 \leq 5000$, $200 \leq D_2 \leq 800$, $5 \leq L_2 / D_2 \leq 15$, $20 \leq n_2 \leq 50$, $3 \leq D_2 / d_{21} \leq 10$, and $9 \leq D_2 / d_{22} \leq 20$,
6. the process according to any one of items 1 to 5, wherein each of said first continuous multi-stage distillation column and said second continuous multi-stage distillation column is a distillation column having a tray and / or a packing as said internal,
7. the process according to item 6, wherein said first continuous multi-stage distillation column is a plate type distillation column having the tray as said internal, and said second continuous multi-stage distillation column is a distillation column having both the packing and the tray as said internal,
8. the process according to item 6 or 7, wherein each tray in said first

continuous multi-stage distillation column and said second continuous multi-stage distillation column is a sieve tray having a sieve portion and a downcomer portion,

9. the process according to item 8, wherein each sieve tray has 100 to 1000 holes / m² in said sieve portion,

10. the process according to item 8 or 9, wherein a cross-sectional area per hole of each sieve tray is in a range of from 0.5 to 5 cm²,

11. the process according to item 6 or 7, wherein said second continuous multi-stage distillation column is a distillation column having, as said internal, the packing in the upper portion of the column, and the tray in the lower portion of the column,

12. the process according to any one of items 6 to 11, wherein said packing of said internal in said second continuous multi-stage distillation column is one or a plurality of sets of structured packings,

13. the process according to item 12, wherein the structured packing in said second continuous multi-stage distillation column is at least one type selected from the group consisting of Mellapak, Gempak, Techno-pack, Flexipac, a Sulzer packing, a Goodroll packing, and Glitschgrid,

14. the process according to any one of items 1 to 13, wherein each of said high boiling point material separating column A and said diphenyl carbonate purifying column B is a distillation column having a tray and/or a packing as said internal,

15. the process according to item 14, wherein the internal of each of said high boiling point material separating column A and said diphenyl carbonate purifying column B is the packing,

16. the process according to item 15, wherein the packing is a structured packing of at least one type selected the group consisting of Mellapak, Gempak, Techno-pack, Flexipac, a Sulzer packing, a Goodroll packing, and Glitschgrid.

17. the process according to any one of items 1 to 16, wherein, the side casing in the polymerization reaction zone is cylindrical with an inside diameter D (cm) and a length L (cm), the tapered bottom casing, which is connected to the lower portion of the side casing, is conical, and the discharge port, which is in the lowermost portion of said conical bottom casing, is cylindrical with an inside diameter d (cm), wherein D , L and d satisfy the following formulae (29), (30), (31) and (32);

$$100 \leq D \leq 1800 \quad (29),$$

$$5 \leq D / d \leq 50 \quad (30),$$

$$0.5 \leq L / D \leq 30 \quad (31), \text{ and}$$

$$h - 20 \leq L \leq h + 300 \quad (32),$$

18. the process according to any one of items 1 to 17, wherein said h satisfies the formula (33);

$$400 < h \leq 2500 \quad (33),$$

19. the process according to any one of items 1 to 18, wherein each guide is cylindrical, or pipe-shaped and made to be such that the molten prepolymer cannot enter therein, with an outside diameter r (cm), wherein r satisfies the formula (34);

$$0.1 \leq r \leq 1 \quad (34),$$

20. the process according to any one of items 1 to 19, wherein the polymerization is carried out using two or more of said guide-contacting downflow type polymerization apparatuses linked together,

21. the process according to any of items 1 to 20, wherein the plurality of the guide-contacting downflow type polymerization apparatuses according to item 17 comprise two polymerization apparatuses being a first guide-contacting downflow type polymerization apparatus and a second guide-contacting downflow type polymerization apparatus, wherein in a process in which a polymerization degree is increased in this order, a total external surface area $S1$ (m^2) of the guides in said first guide-contacting downflow type polymerization apparatus and a total external surface area $S2$ (m^2) of the guides in said second guide-contacting downflow type polymerization apparatus satisfy the formula (35);

$$1 \leq S1 / S2 \leq 20 \quad (35).$$

In addition, according to the second aspect of the present invention, there are provided:

22. a high-quality aromatic polycarbonate produced in an amount of not less than 1 ton / hr, which is produced by the process according to any of items 1 to 21,

23. the high-quality aromatic polycarbonate according to item 22, having a content of alkali metal and / or alkaline earth metal compounds in a range of from 0.1 to 0.01 ppm in terms of metallic elements therein, and a halogen content of not more than 1 ppb,

24. the high-quality aromatic polycarbonate according to item 22 or 23, being an aromatic polycarbonate having a main chain thereof partially branched through a foreign linkage including an ester linkage or an ether linkage, and having a content of said foreign linkage in a range of from 0.05 to 0.5 mol% based on carbonate linkages.

Advantageous Effects of the Invention

It has been discovered that, when producing the aromatic polycarbonate from the dialkyl carbonate and the aromatic dihydroxy compound, by implementing the process according to the present invention which comprises the steps of: (I) producing a diphenyl carbonate using two reactive distillation columns each having a specified structure; (II) purifying the diphenyl carbonate by using a high boiling point material separating column A and a diphenyl carbonate purifying column B each having a specified structure so as to obtain a high-purity diphenyl carbonate from the diphenyl carbonate; (III) subsequent producing an aromatic polycarbonate by using a guide-contacting downflow type polymerization apparatus having a specified structure from a molten prepolymer obtained from an aromatic dihydroxy compound and the high-purity diphenyl carbonate; and (IV) recycling by-produced phenol into the step (I), a high-quality high-performance aromatic polycarbonate having excellent mechanical properties and no discoloration can be produced on an industrial scale of not less than 1 ton / hr at a fast polymerization rate. Moreover, it has been discovered that a high-quality aromatic polycarbonate can be produced stably for a prolonged period of time of, for example not less than 2000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours, with little variation in molecular weight. The present invention thus provides a process that achieves excellent effects as an industrial process for the production of a high-quality aromatic polycarbonate.

Brief Description of Drawings

FIG. 1 is a schematic view of the first continuous reactive distillation column preferable for carrying out the present invention, the distillation column having internals provided in a trunk portion thereof;

FIG. 2 is a schematic drawing of the second continuous reactive distillation column preferable for carrying out the present invention, the distillation column having provided, in a trunk portion thereof, internals comprising structured packings in an upper portion and sieve trays in a lower portion;

FIG. 3 is a schematic view of the apparatus comprising the first continuous reactive distillation column and the second continuous reactive distillation column linked together preferable for carrying out the present invention;

FIG. 4 is a schematic view of the apparatus comprising a high boiling point material separating column A and a diphenyl carbonate purifying column B linked together preferable for carrying out the present invention;

FIG. 5 is a schematic view of the guide-contacting downflow type polymerization apparatus preferable for carrying out the present invention; and

FIG. 6 is a schematic view of the guide-contacting downflow type polymerization apparatus having a cylindrical side casing and a tapered bottom casing preferable for carrying out the present invention.

Description of Reference Numerals

In Figures 1, 2 and 3

1: gas outlet, 2: liquid outlet, 3: inlet, 4: inlet, 5: end plate, L_1 and L_2 : length of trunk portion, D_1 and D_2 : inside diameter of trunk portion, d_{11} and d_{21} : inside diameter of gas outlet (cm), 101: first continuous multi-stage distillation column, 201: second continuous multi-stage distillation column, 11, 12, and 21: inlet, 13 and 23: column top gas outlet, 14, 24, 18 and 28: heat exchanger, 17 and 27: column bottom liquid outlet, 16 and 26: column top component outlet, 31: column bottom component outlet of the second continuous multi-stage distillation column,

In Figure 4

A1 and B1: inlet, B2: outlet, 11: column bottom component outlet of high boiling point material separating column A, 13 and 23: column top gas outlet, 14, 24, 18, 28, and 38: heat exchanger, 15 and 25: reflux liquid inlet, 16: column top component outlet of high boiling point material separating column A, 17 and 27: column bottom liquid outlet, 26: column top component outlet of diphenyl carbonate purifying column B, 31: column bottom component outlet of diphenyl carbonate purifying column B, 33: side cut component outlet of diphenyl carbonate purifying column B

In Figures 5 and 6

1: molten prepolymer receiving port, 2: perforated plate, 3: molten prepolymer feeding zone, 4: guide, 5: polymerization reaction zone, 6: vacuum vent, 7: aromatic polycarbonate discharge port, 8: aromatic polycarbonate discharge pump, 9: inert gas feeding port which is used according to need, 10: side casing of the polymerization reaction zone, 11: tapered bottom casing of the polymerization reaction zone, 12:

outlet of aromatic polycarbonate.

Best Mode for Carrying Out the Invention

Following is a detailed description of the present invention.

In the present invention, first, a step (I) of continuously producing a diphenyl carbonate on an industrial scale from a dialkyl carbonate and a phenol is carried out.

The dialkyl carbonate used in step (I) is a compound represented by the general formula (36);



wherein R^a represents an alkyl group having 1 to 10 carbon atoms, an alicyclic group having 3 to 10 carbon atoms, or an aralkyl group having 6 to 10 carbon atoms. Examples of R^a include alkyl groups 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; alicyclic groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl; and aralkyl groups such as benzyl, phenethyl (isomers), phenylpropyl (isomers), phenylbutyl (isomers) and methylbenzyl (isomers). These alkyl groups, alicyclic groups and aralkyl groups may be substituted with other substituents such as lower alkyl groups, lower alkoxy groups, cyano groups or halogen atoms, and may also contain unsaturated bonds.

Examples of dialkyl carbonates having such an R^a include dimethyl carbonate, diethyl carbonate, dipropyl carbonate (isomers), diphenyl carbonate, dibutenyl carbonate (isomers), dibutyl carbonate

(isomers), dipentyl carbonate (isomers), dihexyl carbonate (isomers), diheptyl carbonate (isomers), dioctyl carbonate (isomers), dinonyl carbonate (isomers), didecyl carbonate (isomers), dicyclopentyl carbonate, dicyclohexyl carbonate, dicycloheptyl carbonate, dibenzyl carbonate, diphenethyl carbonate (isomers), di(phenylpropyl) carbonate (isomers), di(phenylbutyl) carbonate (isomers), di(chlorobenzyl) carbonate (isomers), di(methoxybenzyl) carbonate (isomers), di(methoxymethyl) carbonate, di(methoxyethyl) carbonate (isomers), di(chloroethyl) carbonate (isomers) and di(cyanoethyl) carbonate (isomers).

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

The phenol used in step (I) is one represented by following general formula (37), being a compound in which a hydroxyl group is directly bonded to a phenyl group (Ph). In some cases, a substituted phenol in which the phenyl group is substituted with lower alkyl group(s) or lower alkoxy group(s) may be used.



(37)

The phenol used in the present invention preferably substantially does

not contain a halogen.

The diphenyl carbonate referred to in the present invention is thus one represented by general formula (38);



A molar ratio of the dialkyl carbonate to the phenol used in the starting material in step (I) is preferably in a range of from 0.1 to 10. Outside this range, the amount of unreacted starting material remaining relative to a predetermined amount of the desired diphenyl carbonate produced becomes high, which is not efficient, and moreover much energy is required to recover the starting material. For such reasons, the above molar ratio is more preferably in a range of from 0.5 to 5, yet more preferably from 0.8 to 3, still more preferably from 1 to 2.

In the present invention, not less than 1 ton / hr of the aromatic polycarbonate is continuously produced, and for this, not less than approximately 0.85 ton / hr of high-purity diphenyl carbonate must be continuously produced.

In step (I), the minimum amount of the phenol fed in continuously is thus generally 15 P ton / hr, preferably 13 P ton / hr, more preferably 10 P ton / hr, based on the amount of the aromatic polycarbonate (P ton / hr) to be produced. In a more preferable case, this amount can be made to be less than 8 P ton / hr.

The dialkyl carbonate and the phenol used in the starting material in step (I) may each be of high purity, or may contain other compounds, for example may contain compounds or reaction by-products produced in a first continuous multi-stage distillation column and / or a second continuous multi-stage distillation column, described below. In the case

of industrial implementation, for the starting material, besides fresh dialkyl carbonate and phenol newly introduced into the reaction system, it is also preferable to use dialkyl carbonate and / or phenol recovered from the first continuous multi-stage distillation column and / or the second continuous multi-stage distillation column. In the process according to the present invention, column top components constituting a low boiling point reaction mixture from the second continuous multi-stage distillation column are fed into the first continuous multi-stage distillation column. Here, the second column low boiling point reaction mixture may be fed into the first continuous multi-stage distillation column as is, or after some of the components thereof have been separated out.

Accordingly, in the present invention, which is implemented industrially, it is preferable for the starting material fed into the first continuous multi-stage distillation column to contain any of an alcohol, an alkyl phenyl carbonate, the diphenyl carbonate, an alkyl phenyl ether, and so on. A starting material further containing small amounts of high boiling point by-products such as Fries rearrangement products of the alkyl phenyl carbonate and diphenyl carbonate which are the products, derivatives thereof, and so on can also be preferably used. In the present invention, in the case, for example, of producing methyl phenyl carbonate and diphenyl carbonate using a starting material containing dimethyl carbonate as the dialkyl carbonate and unsubstituted phenol as the phenol, it is preferable for this starting material to contain methanol, and methyl phenyl carbonate and diphenyl carbonate, which are the reaction products, and the starting material may further contain small amounts of anisole, phenyl salicylate and methyl salicylate, which are

reaction by-products, and high boiling point by-products derived therefrom.

Furthermore, most of the phenol used in step (I) consists of the phenol by-produced in step (III) of the present invention. This by-produced phenol must be circulated back into step (I) through step (IV).

The diphenyl carbonate produced in step (I) is obtained through transesterification between the dialkyl carbonate and the phenol. Included under this transesterification are a reaction in which one or both of the alkoxy groups of the dialkyl carbonate is / are exchanged with the phenoxy group of the phenol and an alcohol is eliminated, and a reaction in which two molecules of the alkyl phenyl carbonate produced are converted into the diphenyl carbonate and the dialkyl carbonate through a transesterification reaction therebetween, i.e. a disproportionation reaction. In step (I), in the first continuous multi-stage distillation column, the alkyl phenyl carbonate is mainly obtained, and in the second continuous multi-stage distillation column, the diphenyl carbonate and the dialkyl carbonate are mainly obtained through the disproportionation reaction of the alkyl phenyl carbonate. The diphenyl carbonate obtained in step (I) does not contain a halogen at all, and hence is important as a starting material when industrially producing the aromatic polycarbonate in the present invention. The reason for this is that if a halogen is present in the starting material for the polymerization even in a small amount of less than 1 ppm, then this may impede the polymerization reaction, thus impeding stable production of the aromatic polycarbonate, or cause a deterioration of the properties of, or discoloration of, the

aromatic polycarbonate produced.

As a catalyst used in the first continuous multi-stage distillation column and / or the second continuous multi-stage distillation column in step (I), for example, a metal-containing compound selected from the following compounds can be used:

<Lead compounds>

lead oxides such as PbO , PbO_2 and Pb_3O_4 ;

lead sulfides such as PbS and Pb_2S ;

lead hydroxides such as $\text{Pb}(\text{OH})_2$ and $\text{Pb}_2\text{O}_2(\text{OH})_2$;

plumbites such as Na_2PbO_2 , K_2PbO_2 , NaHPbO_2 and KHPbO_2 ;

plumbates such as Na_2PbO_3 , $\text{Na}_2\text{H}_2\text{PbO}_4$, K_2PbO_3 , $\text{K}_2[\text{Pb}(\text{OH})_6]$, K_4PbO_4 , Ca_2PbO_4 and CaPbO_3 ;

lead carbonates and basic salts thereof such as PbCO_3 and $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$;

lead salts of organic acids, and carbonates and basic salts thereof, such as $\text{Pb}(\text{OCOCH}_3)_2$, $\text{Pb}(\text{OCOCH}_3)_4$ and $\text{Pb}(\text{OCOCH}_3)_2 \cdot \text{PbO} \cdot 3\text{H}_2\text{O}$;

organolead compounds such as Bu_4Pb , Ph_4Pb , Bu_3PbCl , Ph_3PbBr , Ph_3Pb (or Ph_6Pb_2), Bu_3PbOH and Ph_3PbO (wherein Bu represents a butyl group, and Ph represents a phenyl group);

alkoxylead compounds and aryloxylead compounds such as $\text{Pb}(\text{OCH}_3)_2$, $(\text{CH}_3\text{O})\text{Pb}(\text{OPh})$ and $\text{Pb}(\text{OPh})_2$;

lead alloys such as Pb-Na, Pb-Ca, Pb-Ba, Pb-Sn and Pb-Sb;

lead minerals such as galena and zinc blende; and

hydrates of such lead compounds;

<Copper family metal compounds>

salts and complexes of copper family metals such as CuCl , CuCl_2 ,

CuBr, CuBr₂, CuI, CuI₂, Cu(OAc)₂, Cu(acac)₂, copper oleate, Bu₂Cu, (CH₃O)₂Cu, AgNO₃, AgBr, silver picrate, AgC₆H₅ClO₄, [AuC≡C-C(CH₃)₃]_n and [Cu(C₇H₈)Cl]₄ (wherein acac represents an acetylacetone chelate ligand);

<Alkali metal complexes>

alkali metal complexes such as Li(acac) and LiN(C₄H₉)₂;

<Zinc complexes>

zinc complexes such as Zn(acac)₂;

<Cadmium complexes>

cadmium complexes such as Cd(acac)₂;

<Iron family metal compounds>

complexes of iron family metals such as Fe(C₁₀H₈)(CO)₅, Fe(CO)₅, Fe(C₄H₆)(CO)₃, Co(mesitylene)₂, (PEt₂Ph)₂, CoC₅F₅(CO)₇, Ni-π-C₅H₅NO and ferrocene;

<Zirconium complexes>

zirconium complexes such as Zr(acac)₄ and zirconocene;

<Lewis acid type compounds>

Lewis acids and Lewis acid-forming transition metal compounds such as AlX₃, TiX₃, TiX₄, VOX₃, VX₅, ZnX₂, FeX₃ and SnX₄ (wherein X represents a halogen atom, an acetoxy group, an alkoxy group or an aryloxy group); and

<Organo-tin compounds>

organo-tin compounds such as (CH₃)₃SnOCOCH₃, (C₂H₅)₃SnOCOC₆H₅, Bu₃SnOCOCH₃, Ph₃SnOCOCH₃, Bu₂Sn(OCOCH₃)₂, Bu₂Sn(OCOC₁₁H₂₃)₂, Ph₃SnOCH₃, (C₂H₅)₃SnOPh, Bu₂Sn(OCH₃)₂, Bu₂Sn(OC₂H₅)₂, Bu₂Sn(OPh)₂, Ph₂Sn(OCH₃)₂, (C₂H₅)₃SnOH, Ph₃SnOH,

Bu_2SnO , $(\text{C}_8\text{H}_{17})_2\text{SnO}$, Bu_2SnCl_2 and $\text{BuSnO}(\text{OH})$.

Each of these catalysts must be a soluble catalyst that dissolves in the reaction system (a homogeneous catalyst).

Each of these catalyst components may of course have been reacted with an organic compound present in the reaction system such as an aliphatic alcohol, the phenol, the aromatic polycarbonate, the diphenyl carbonate or the dialkyl carbonate, or may have been subjected to heating treatment with the starting material or products prior to the reaction.

The catalyst used in step (I) is preferably one having a high solubility in the reaction liquid under the reaction conditions. Examples of preferable catalysts in this sense include PbO , $\text{Pb}(\text{OH})_2$ and $\text{Pb}(\text{OPh})_2$; TiCl_4 , $\text{Ti}(\text{OMe})_4$, $(\text{MeO})\text{Ti}(\text{OPh})_3$, $(\text{MeO})_2\text{Ti}(\text{OPh})_2$, $(\text{MeO})_3\text{Ti}(\text{OPh})$ and $\text{Ti}(\text{OPh})_4$; SnCl_4 , $\text{Sn}(\text{OPh})_4$, Bu_2SnO and $\text{Bu}_2\text{Sn}(\text{OPh})_2$; FeCl_3 , $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OPh})_3$; and such catalysts that have been treated with phenol, the reaction liquid or the like. The catalyst used in the first continuous multi-stage distillation column and the catalyst used in the second continuous multi-stage distillation column may be the same as one another, or different.

The first continuous multi-stage distillation column used in step (I) comprises a structure having a cylindrical trunk portion having a length L_1 (cm) and an inside diameter D_1 (cm), and having internals with number of stages n_1 therein, and has a gas outlet having an inside diameter d_{11} (cm) at a top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_{12} (cm) at a bottom of the column or in a lower portion of the column near to the bottom, at

least one first inlet provided in the upper portion and / or a middle portion of the column below the gas outlet, and at least one second inlet provided in the middle portion and / or the lower portion of the column above the liquid outlet, wherein L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} must satisfy the formulae (1) to (6) respectively;

$$1500 \leq L_1 \leq 8000 \quad (1)$$

$$100 \leq D_1 \leq 2000 \quad (2)$$

$$2 \leq L_1 / D_1 \leq 40 \quad (3)$$

$$20 \leq n_1 \leq 120 \quad (4)$$

$$5 \leq D_1 / d_{11} \leq 30 \quad (5) \text{ and}$$

$$3 \leq D_1 / d_{12} \leq 20 \quad (6).$$

Moreover, the second continuous multi-stage distillation column used in step (I) comprises a structure having a cylindrical trunk portion having a length L_2 (cm) and an inside diameter D_2 (cm), and having internals with number of stages n_2 thereinside, and has a gas outlet having an inside diameter d_{21} (cm) at a top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_{22} (cm) at a bottom of the column or in a lower portion of the column near to the bottom, at least one third inlet provided in the upper portion and/or a middle portion of the column below the gas outlet, and at least one fourth inlet provided in the middle portion and/or the lower portion of the column above the liquid outlet, wherein L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} , and D_2 / d_{22} must satisfy the formulae (7) to (12) respectively;

$$1500 \leq L_2 \leq 8000 \quad (7)$$

$$100 \leq D_2 \leq 2000 \quad (8)$$

$$2 \leq L_2 / D_2 \leq 40 \quad (9)$$

$$10 \leq n_2 \leq 80 \quad (10)$$

$$2 \leq D_2 / d_{21} \leq 15 \quad (11) \text{ and}$$

$$5 \leq D_2 / d_{22} \leq 30 \quad (12).$$

It has been discovered that by using the first continuous multi-stage distillation column and the second continuous multi-stage distillation column that simultaneously satisfy the formulae (1) to (12), the diphenyl carbonate can be produced from the dialkyl carbonate and the phenol on an industrial scale of not less than approximately 0.85 ton / hr, preferably not less than 1 ton / hr, 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. The reason why it has become possible to produce such an aromatic 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 composite effect brought about when the conditions of formulae (1) to (12) are combined. Preferable ranges for the respective factors for the continuous multi-stage distillation columns used in step (I) are described below.

If L_1 (cm) or L_2 (cm) is less than 1500, then the conversion decreases and hence it is not possible to attain the desired production amount. Moreover, to keep down the equipment cost while securing the conversion enabling the desired production amount to be attained, L_1 and L_2 must each be made to be not more than 8000. More preferable ranges for L_1 (cm) and L_2 (cm) are respectively $2000 \leq L_1 \leq 6000$ and $2000 \leq L_2 \leq 6000$, with $2500 \leq L_1 \leq 5000$ and $2500 \leq L_2 \leq 5000$ being yet more preferable.

If D_1 (cm) or D_2 (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_1 and D_2 must each be made to be not more than 2000. More preferable ranges for D_1 (cm) and D_2 (cm) are respectively $150 \leq D_1 \leq 1000$ and $150 \leq D_2 \leq 1000$, with $200 \leq D_1 \leq 800$ and $200 \leq D_2 \leq 800$ being yet more preferable.

For the first continuous multi-stage distillation column and the second continuous multi-stage distillation column, so long as D_1 and D_2 are within the above ranges, each of the columns may have the same inside diameter from the upper portion thereof to the lower portion thereof, or the inside diameter may differ for different portions. For example, for each of the continuous multi-stage distillation columns, the inside diameter of the upper portion of the column may be smaller than, or larger than, the inside diameter of the lower portion of the column.

If L_1 / D_1 or L_2 / D_2 is less than 2 or greater than 40, then stable operation becomes difficult. In particular, if L_1 / D_1 or L_2 / D_2 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. More preferable ranges for L_1 / D_1 and L_2 / D_2 are respectively $3 \leq L_1 / D_1 \leq 30$ and $3 \leq L_2 / D_2 \leq 30$, with $5 \leq L_1 / D_1 \leq 15$ and $5 \leq L_2 / D_2 \leq 15$ being yet more preferable.

If n_1 is less than 20, then the conversion decreases and it is not possible to attain the desired production amount for the first continuous

multi-stage distillation column. Moreover, to keep down the equipment cost while securing the conversion enabling the desired production amount to be attained, n_1 must be made to be not more than 120. Furthermore, if n_1 is greater than 120, then the pressure difference between the top and bottom of the column becomes too great, and hence prolonged stable operation of the first continuous multi-stage distillation column 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_1 is $30 \leq n_1 \leq 100$, with $40 \leq n_1 \leq 90$ being yet more preferable.

Moreover, if n_2 is less than 10, then the conversion decreases and it is not possible to attain the desired production amount for the second continuous multi-stage distillation column. Moreover, to keep down the equipment cost while securing the conversion enabling the desired production amount to be attained, n_2 must be made to be not more than 80. Furthermore, if n_2 is greater than 80, then the pressure difference between the top and bottom of the column becomes too great, and hence prolonged stable operation of the second continuous multi-stage distillation column 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_2 is $15 \leq n_2 \leq 60$, with $20 \leq n_2 \leq 50$ being yet more preferable.

If D_1 / d_{11} is less than 5, then the equipment cost for the first continuous multi-stage distillation column becomes high. Moreover,

large amounts of gaseous components are readily released to the outside of the system, and hence stable operation of the first continuous multi-stage distillation column becomes difficult. If D_1 / d_{11} is greater than 30, then the gaseous component withdrawal amount becomes relatively low, and hence stable operation becomes difficult, and moreover a decrease in the conversion is brought about. A more preferable range for D_1 / d_{11} is $8 \leq D_1 / d_{11} \leq 25$, with $10 \leq D_1 / d_{11} \leq 20$ being yet more preferable. Furthermore, if D_2 / d_{21} is less than 2, then the equipment cost for the second continuous multi-stage distillation column becomes high. Moreover, large amounts of gaseous components are readily released to the outside of the system, and hence stable operation of the second continuous multi-stage distillation column becomes difficult. If D_2 / d_{21} 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 conversion is brought about. A more preferable range for D_2 / d_{21} is $5 \leq D_2 / d_{21} \leq 12$, with $3 \leq D_2 / d_{21} \leq 10$ being yet more preferable.

If D_1 / d_{12} is less than 3, then the equipment cost for the first continuous multi-stage distillation column becomes high. Moreover, the liquid withdrawal amount becomes relatively high, and hence stable operation of the first continuous multi-stage distillation column becomes difficult. If D_1 / d_{12} is greater than 20, then the flow rate through the liquid outlet and piping becomes excessively fast, and hence erosion becomes liable to occur, bringing about corrosion of the apparatus. A more preferable range for D_1 / d_{12} is $5 \leq D_1 / d_{12} \leq 18$, with $7 \leq D_1 / d_{12} \leq 15$ being yet more preferable. Furthermore, if D_2 / d_{22} is less than 5,

then the equipment cost for the second continuous multi-stage distillation column becomes high. Moreover, the liquid withdrawal amount becomes relatively high, and hence stable operation of the second continuous multi-stage distillation column becomes difficult. If D_2 / d_{22} is greater than 30, then the flow rate through the liquid outlet and piping becomes excessively fast, and hence erosion becomes liable to occur, bringing about corrosion of the apparatus. A more preferable range for D_2 / d_{22} is $7 \leq D_2 / d_{22} \leq 25$, with $9 \leq D_2 / d_{22} \leq 20$ being yet more preferable.

Furthermore, it has been found that in step (I) it is further preferable for the d_{11} and the d_{12} to satisfy the formula (27), and for the d_{21} and the d_{22} to satisfy the formula (28);

$$1 \leq d_{12} / d_{11} \leq 5 \quad (27) \text{ and}$$

$$1 \leq d_{21} / d_{22} \leq 6 \quad (28).$$

The term "prolonged stable operation" for step (I) means that operation can be carried out continuously in a steady state based on the operating conditions with no flooding, clogging of piping, erosion or the like for not less than 1000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours, and a predetermined amount of the diphenyl carbonate can be produced while maintaining high selectivity.

A characteristic feature for step (I) is that the diphenyl carbonate can be produced stably for a prolonged period of time with high selectivity and with a high productivity of not less than 1 ton / hr, preferably not less than 2 ton / hr, more preferably not less than 3 ton / hr. Moreover, another characteristic feature for step (I) is that in the case that L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} for the first continuous

multi-stage distillation column satisfy respectively $2000 \leq L_1 \leq 6000$, $150 \leq D_1 \leq 1000$, $3 \leq L_1 / D_1 \leq 30$, $30 \leq n_1 \leq 100$, $8 \leq D_1 / d_{11} \leq 25$, and $5 \leq D_1 / d_{12} \leq 18$, and L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} , and D_2 / d_{22} for the second continuous multi-stage distillation column satisfy respectively $2000 \leq L_2 \leq 6000$, $150 \leq D_2 \leq 1000$, $3 \leq L_2 / D_2 \leq 30$, $15 \leq n_2 \leq 60$, $2.5 \leq D_2 / d_{21} \leq 12$, and $7 \leq D_2 / d_{22} \leq 25$, not less than 2 ton / hr, preferably not less than 2.5 ton / hr, more preferably not less than 3 ton / hr of the diphenyl carbonate can be produced.

Furthermore, another characteristic feature for step (I) is that in the case that L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} for the first continuous multi-stage distillation column satisfy respectively $2500 \leq L_1 \leq 5000$, $200 \leq D_1 \leq 800$, $5 \leq L_1 / D_1 \leq 15$, $40 \leq n_1 \leq 90$, $10 \leq D_1 / d_{11} \leq 25$, and $7 \leq D_1 / d_{12} \leq 15$, and L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} , and D_2 / d_{22} for the second continuous multi-stage distillation column satisfy respectively $2500 \leq L_2 \leq 5000$, $200 \leq D_2 \leq 800$, $5 \leq L_2 / D_2 \leq 10$, $20 \leq n_2 \leq 50$, $3 \leq D_2 / d_{21} \leq 10$, and $9 \leq D_2 / d_{22} \leq 20$, not less than 3 ton / hr, preferably not less than 3.5 ton / hr, more preferably not less than 4 ton / hr of the diphenyl carbonate can be produced.

The "selectivity" for the diphenyl carbonate in step (I) is based on the phenol reacted. In step (I), a high selectivity of not less than 95% can generally be attained, preferably not less than 97%, more preferably not less than 98%.

Each of the first continuous multi-stage distillation column and the second continuous multi-stage distillation column used in step (I) is preferably a distillation column having trays and/or packings 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. Examples of the trays include a bubble-cap tray, a sieve tray, a valve tray, a counterflow tray, a Superfrac tray, a Maxfrac tray, or the like. Examples of the packing include 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-pack, Flexipac, a Sulzer packing, a Goodroll packing or Glitschgrid. The multi-stage distillation column having both a tray portion and a portion packed with packings can also be used. Furthermore, the term "number of stages n of the internal" used in the present invention means the number of trays in the case of the tray, and the theoretical number of stages in the case of packing. In the case of the multi-stage distillation column having both the tray portion and the portion packed with packings, n is thus the sum of the number of trays and the theoretical number of stages.

In step (I), in the first continuous multi-stage distillation column, a reaction in which the alkyl phenyl carbonate is produced from the dialkyl carbonate and the phenol mainly occurs. This reaction has an extremely low equilibrium constant, and the reaction rate is slow, and hence it has been discovered that a plate type distillation column having trays as the internal is particularly preferable as the first continuous multi-stage distillation column used in the reactive distillation. Moreover, in the second continuous multi-stage distillation column, it is mainly a disproportionation reaction of the alkyl phenyl carbonate that occurs. This reaction also has a low equilibrium constant, and a slow reaction

rate. Even so, it has been discovered that a distillation column having both packings and trays as the internal is preferable as the second continuous multi-stage distillation column used in the reactive distillation. Furthermore, it has been discovered that a distillation column having the packings installed in the upper portion thereof and trays installed in the lower portion thereof is preferable as the second continuous multi-stage distillation column. It has been discovered that the packings in the second continuous multi-stage distillation column are preferably structured packings, and that of structured packings, Mellapak is particularly preferable.

Furthermore, it has been discovered that, as each of the trays installed in the first continuous multi-stage distillation column and the second continuous multi-stage distillation column, a sieve tray having a sieve portion and a downcomer portion is particularly good in terms of the relationship between performance and equipment cost. It has also been discovered that each 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 each 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 each 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 continuous multi-stage distillation columns, the object of

the present invention can be attained more easily.

When carrying out step (I), the diphenyl carbonate is continuously produced by continuously feeding the dialkyl carbonate and the phenol constituting the starting material into the first continuous multi-stage distillation column in which the catalyst is present, carrying out reaction and distillation simultaneously in the first column, continuously withdrawing a first column low boiling point reaction mixture containing a produced alcohol from an upper portion of the first column in a gaseous form, continuously withdrawing a first column high boiling point reaction mixture containing a produced alkyl phenyl carbonate from a lower portion of the first column in a liquid form, continuously feeding the first column high boiling point reaction mixture into the second continuous multi-stage distillation column in which the catalyst is present, carrying out reaction and distillation simultaneously in the second column, continuously withdrawing a second column low boiling point reaction mixture containing a produced dialkyl carbonate from an upper portion of the second column in a gaseous form, continuously withdrawing a second column high boiling point reaction mixture containing a produced diphenyl carbonate from a lower portion of the second column in a liquid form, and continuously feeding the second column low boiling point reaction mixture containing the dialkyl carbonate into the first continuous multi-stage distillation column.

As mentioned earlier, the starting material may contain the alcohol, the alkyl phenyl carbonate and the diphenyl carbonate that are reaction products, and reaction by-products such as an alkyl phenyl ether and high boiling point compounds. Considering the equipment and cost

required for separation and purification in other processes, when actually implementing the present invention industrially, it is preferable for the starting material to contain small amounts of such compounds.

In step (I), when continuously feeding the dialkyl carbonate and the phenol constituting the starting material into the first continuous multi-stage distillation column, this starting material may be fed into the first distillation column in a liquid form and / or a gaseous form from inlet(s) provided in one or a plurality of positions in the upper portion or the middle portion of the first distillation column below the gas outlet in the upper portion of the first distillation column. It is also preferable to feed the starting material containing a large proportion of the phenol into the first distillation column in a liquid form from an inlet provided in the upper portion of the first distillation column, and feed the starting material containing a large proportion of the dialkyl carbonate into the first distillation column in a gaseous form from an inlet provided in the lower portion of the first distillation column above the liquid outlet in the lower portion of the first distillation column.

Moreover, in step (I), the first column high boiling point reaction mixture containing the alkyl phenyl carbonate continuously withdrawn from the lower portion of the first continuous multi-stage distillation column is continuously fed into the second continuous multi-stage distillation column. Here, the first column high boiling point reaction mixture is preferably fed into the second distillation column in a liquid form and / or a gaseous form from inlet(s) provided in one or a plurality of positions in the upper portion or the central portion of the second distillation column below the gas outlet in the upper portion of the second

distillation column. Moreover, in the case of using, as the second distillation column, 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 of the present invention, it is preferable for at least one position where an inlet is provided to be between the packing portion and the tray portion. Moreover, in the case that the packings comprise a plurality of sets of structured packings, it is preferable for an inlet to be installed in a space between the sets of structured packings.

Moreover, in step (I), it is also preferable to carry out a reflux operation of condensing the gaseous component withdrawn from the top of each of the first continuous multi-stage distillation column and the second continuous multi-stage distillation column, and then returning some of this component into the upper portion of that distillation column. In this case, the reflux ratio for the first continuous multi-stage distillation column is in a range of from 0 to 10, and the reflux ratio for the second continuous multi-stage distillation column is in a range of from 0.01 to 10, preferably from 0.08 to 5, more preferably from 0.1 to 2. For the first continuous multi-stage distillation column, not carrying out such a reflux operation (i.e. reflux ratio = 0) is also a preferable embodiment.

In step (I), the method of making the homogeneous catalyst be present in the first continuous multi-stage distillation column may be any method. It is preferable to feed the catalyst into the first distillation column from a position above the middle portion of the first distillation column. In this case, a catalyst solution obtained by dissolving the catalyst 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. The amount of the catalyst used in the first continuous multi-stage distillation column in the present invention varies depending on the type of catalyst used, 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 0.0005 to 10 % by weight, more preferably from 0.001 to 1 % by weight, based on the total mass of the starting material.

Moreover, in step (I), the method of making the catalyst be present in the second continuous multi-stage distillation column may be any method. In the case that the catalyst is a solid that is insoluble in the reaction liquid, it is preferable for the catalyst to be fixed inside the column by, for example, being installed on stages inside the second continuous multi-stage distillation column or being installed in the form of a packing. In the case of a catalyst that dissolves in the starting material or the reaction liquid, it is preferable to feed the catalyst into the second distillation column from a position above the central portion of the second distillation column. In this case, a catalyst solution obtained by dissolving the catalyst 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. The amount of the catalyst used in the second continuous multi-stage distillation column in the present invention varies depending on the type of catalyst used, 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 0.0005 to 10 % by weight, more preferably from 0.001 to 1 % by weight, based on the total mass of the starting material.

In step (I), the catalyst used in the first continuous multi-stage distillation column and the catalyst used in the second continuous multi-stage distillation column may be the same or different, but are preferably the same. More preferably, the same catalyst is used in both columns, this catalyst being one that dissolves in the reaction liquid in both columns. In this case, the catalyst dissolved in the high boiling point reaction mixture in the first continuous multi-stage distillation column is generally withdrawn from the lower portion of the first distillation column together with the alkyl phenyl carbonate and so on, and fed into the second continuous multi-stage distillation column as is; this is a preferable embodiment. If necessary, more of the catalyst can be newly added into the second continuous multi-stage distillation column.

The reaction times for the transesterification reactions carried out in step (I) are considered to equate to the average residence times of the reaction liquids in the first continuous multi-stage distillation column and the second continuous multi-stage distillation column. Each of these reaction times varies depending on the form of the internals in that 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 in each of the first

continuous multi-stage distillation column and the second continuous multi-stage distillation column is generally in a range of from 0.01 to 10 hours, preferably from 0.05 to 5 hours, more preferably from 0.1 to 3 hours.

The reaction temperature in the first continuous multi-stage distillation column varies depending on the type of the starting material compounds used, and the type and amount of the catalyst. This 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 an alkyl phenyl ether increases, which is undesirable. For this reason, the reaction temperature in the first continuous multi-stage distillation column is preferably in a range of from 130 to 280°C, more preferably from 150 to 260°C, yet more preferably from 180 to 250°C.

The reaction temperature in the second continuous multi-stage distillation column varies depending on the type of the starting material compounds used, and the type and amount of the catalyst. This 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 an alkyl phenyl ether, and Fries rearrangement products of the starting material compounds and the produced diphenyl carbonate, and derivatives thereof increases, which is undesirable. For

this reason, the reaction temperature in the second continuous multi-stage distillation column is preferably in a range of from 130 to 280°C, more preferably from 150 to 260°C, yet more preferably from 180 to 250°C.

Moreover, the reaction pressure in the first continuous multi-stage distillation column 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 first continuous multi-stage distillation column may be at any of a reduced pressure, normal pressure, or an applied pressure. The pressure at the top of the column is generally in a range of from 0.1 to 2×10^7 Pa, preferably from 10^5 to 10^7 Pa, more preferably from 2×10^5 to 5×10^6 Pa.

The reaction pressure in the second continuous multi-stage distillation column 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 second continuous multi-stage distillation column may be at any of a reduced pressure, normal pressure, or an applied pressure. The pressure at the top of the column 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.

Furthermore, as the first continuous multi-stage distillation column in step (I), a plurality of distillation columns may be used. In this case, the distillation columns may be linked together in series, in parallel, or in a combination of series and parallel. Moreover, as the second continuous multi-stage distillation column in step (I), a plurality of distillation columns may be used. In this case, the distillation columns

may be linked together in series, in parallel, or in a combination of series and parallel.

The material constituting each of the first continuous multi-stage distillation column and the second continuous multi-stage distillation column used in step (I) is generally a metallic material such as carbon steel or stainless steel. In terms of the quality of the aromatic carbonates produced, stainless steel is preferable.

The second column high boiling point reaction mixture continuously withdrawn from the lower portion of the second continuous multi-stage distillation column in a liquid form in step (I) has the diphenyl carbonate as a main component thereof, but in addition to the diphenyl carbonate, generally also contains the catalyst component, unreacted starting material, the alkyl phenyl carbonate, and by-products. As the by-products, there are by-products having a relatively low boiling point such as an alkyl phenyl ether, and high boiling point by-products such as Fries rearrangement products of the alkyl phenyl carbonate and diphenyl carbonate and derivatives thereof, and degeneration products of the diphenyl carbonate. For example, in the case of producing diphenyl carbonate using dimethyl carbonate and phenol as the starting material, anisole, methyl salicylate, phenyl salicylate, xanthone, phenyl methoxybenzoate, 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene, and so on are present as reaction by-products, and a small amount of high boiling point by-products thought to be produced through further reaction of these reaction by-products is generally also contained.

It is thus necessary to carry out a purification step (II) for obtaining a high-purity diphenyl carbonate from the second column high

boiling point reaction mixture. In step (II), processes that could be used for obtaining the high-purity diphenyl carbonate from the second column high boiling point reaction mixture include, for example, distillation and / or recrystallization, but of these, in the present invention, it has been discovered that carrying out step (II) using a distillation process is preferable. Furthermore, in the present invention, it has been discovered that by using two distillation columns in step (II), i.e. a high boiling point material separating column A, and a diphenyl carbonate purifying column B having a side cut outlet, the high-purity diphenyl carbonate can be obtained efficiently with a high yield as a side cut component.

In step (II), the second column high boiling point reaction mixture is continuously introduced into the high boiling point material separating column A, and separation is carried out continuously into a column top component A_T containing the diphenyl carbonate and a column bottom component A_B containing catalyst, the column top component A_T is then continuously introduced into the diphenyl carbonate purifying column B having the side cut outlet, and separation by distillation is carried out continuously into three components, i.e. a column top component B_T , a side cut component B_S , and a column bottom component B_B , the high-purity diphenyl carbonate being obtained continuously as the side cut component B_S in an amount of not less than 0.85 ton / hr, preferably not less than 1 ton / hr. To achieve this, the high boiling point material separating column A and the diphenyl carbonate purifying column B must be used in combination, each being made to be a continuous multi-stage distillation column having a specified structure.

The second column high boiling point reaction mixture obtained from step (I) generally contains 50 to 80 % by weight of the diphenyl carbonate, and hence to obtain not less than 1 ton / hr of the high-purity diphenyl carbonate, the amount of the reaction mixture continuously introduced into the high boiling point material separating column A is not less than approximately 1.3 to 2 ton / hr, this amount varying depending on the diphenyl carbonate content. It is generally necessary to subject more than approximately 2 ton / hr of the reaction mixture to the separation and purification.

The high boiling point material separating column A used in step (II) must be a continuous multi-stage distillation column having a length L_A (cm) and an inside diameter D_A (cm), and having internals with number of stages n_A therein, wherein L_A , D_A , and n_A satisfy the following formulae (13) to (15);

$$800 \leq L_A \leq 3000 \quad (13)$$

$$100 \leq D_A \leq 1000 \quad (14) \text{ and}$$

$$20 \leq n_A \leq 100 \quad (15).$$

Moreover, the diphenyl carbonate purifying column B used in step (II) must be a continuous multi-stage distillation column having a length L_B (cm) and an inside diameter D_B (cm), having internals therein, having an inlet B1 at a middle stage of the column, and a side cut outlet B2 between the inlet B1 and the column bottom, and having number of stages n_{B1} of the internals above the inlet B1, number of stages n_{B2} of the internals between the inlet B1 and the side cut outlet B2, number of stages n_{B3} of the internals below the side cut outlet B2, and a total number of stages $n_B (= n_{B1} + n_{B2} + n_{B3})$, wherein L_B , D_B , n_{B1} , n_{B2} , n_{B3} , and

n_B satisfy following the formulae (16) to (21);

$$1000 \leq L_B \leq 5000 \quad (16)$$

$$100 \leq D_B \leq 1000 \quad (17)$$

$$5 \leq n_{B1} \leq 20 \quad (18)$$

$$12 \leq n_{B2} \leq 40 \quad (19)$$

$$3 \leq n_{B3} \leq 15 \quad (20) \text{ and}$$

$$20 \leq n_B \leq 70 \quad (21).$$

It has been discovered that by using the high boiling point material separating column A and the diphenyl carbonate purifying column B simultaneously satisfying all of these conditions, the high-purity diphenyl 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 diphenyl carbonate-containing reaction mixture (the second column high boiling point reaction mixture from step (I)) that has been obtained through transesterification with the dialkyl carbonate and the phenol as the starting material in the presence of a homogeneous catalyst. The reason why it has become possible to produce the high-purity diphenyl carbonate on an industrial scale with such excellent effects by implementing the process according to the present invention is not clear, but this is supposed to be due to a composite effect brought about when the conditions of the formulae (13) to (21) are combined. Preferable ranges for the respective factors are described below.

It is undesirable for L_A (cm) to be less than 800, since then the height over which internals can be installed in the high boiling point material separating column A 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.

As distillation conditions for the high boiling point material separating column A in step (II), it is preferable for a column bottom temperature T_A to be in a range of from 185 to 280°C, and a column top pressure P_A to be in a range of from 1000 to 20000 Pa. It is undesirable for T_A 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_A to be greater 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 less than 1000 Pa, since then large equipment enabling a high vacuum to be maintained must be used. Moreover, it is undesirable for P_A to be greater than 20000 Pa, since then the distillation temperature must be 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.

It is undesirable for L_B (cm) to be less than 1000 , since then the height over which internals can be installed in the diphenyl carbonate purifying column B 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 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 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 diphenyl carbonate purifying column B 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_B is $25 \leq n_B \leq 55$, with $30 \leq n_B \leq 50$ being yet more preferable. Furthermore, it has been discovered that to obtain the desired high-purity diphenyl carbonate stably for a prolonged period of time, n_{B1} , n_{B2} , and n_{B3} must be in the ranges $5 \leq n_{B1} \leq 20$, $12 \leq n_{B2} \leq 40$, and $3 \leq n_{B3} \leq 15$ respectively. More preferable ranges are $7 \leq n_{B1} \leq 15$, $12 \leq n_{B2} \leq 30$, and $3 \leq n_{B3} \leq 10$.

As distillation conditions for the diphenyl carbonate purifying column B in step (II), it is preferable for the column bottom temperature T_B to be in a range of from 185 to 280°C, and a column top pressure P_B to be in a range of from 1000 to 20000 Pa. 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.

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

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

Each of the high boiling point material separating column A and the diphenyl carbonate purifying column B used in step (II) is a distillation column having trays and/or packings as the internal. The term "internal" used in the present invention means a part in the distillation column where gas and liquid are actually brought into contact with one another. As the tray, ones as described in the section on step (I) are preferable. Moreover, the term "number of stages of the internal" has the same meaning as defined above.

It has been discovered that for step (II), the high boiling point material separating column A preferably has the packings as the internal, and furthermore structured packings are preferable as these packings. Moreover, it has been discovered that the diphenyl carbonate purifying column B preferably has packings as the internal, particularly preferably one set or a plurality of sets of structured packings.

The high boiling point reaction mixture continuously withdrawn

from the bottom of the second reactive distillation column of step (I) generally contains 0.05 to 2 % by weight of the dialkyl carbonate, 1 to 20 % by weight of the phenol, 0.05 to 2 % by weight of an alkyl phenyl ether, 10 to 45 % by weight of the alkyl phenyl carbonate, 50 to 80 % by weight of the diphenyl carbonate, 0.1 to 5 % by weight of high boiling point by-products, and 0.001 to 5 % by weight of the catalyst, and hence this continuously withdrawn column bottom liquid is preferably continuously fed as is into the high boiling point material separating column A of step (II).

The composition of the reaction mixture varies depending on the conditions of the transesterification between the dialkyl carbonate and the phenol, the type and amount of the catalyst, and so on, but so long as the transesterification is carried out under constant conditions, a reaction mixture of approximately constant composition can be produced, and hence the composition of the reaction mixture fed into the high boiling point material separating column A is approximately constant. Nevertheless, in step (II), so long as the composition of the 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 step (II) of the present invention.

In step (II), when continuously feeding the column bottom liquid from the second reactive distillation column of step (I) into the high boiling point material separating column A, this column bottom liquid may be fed in as a liquid from inlet(s) provided in one or a plurality of positions below a middle portion of the separating column A, or it is also

preferable to feed the column bottom liquid from the second reactive distillation column into the separating column A via a reboiler of the separating column A from a conduit provided at a lower portion of the reboiler. The amount of the column bottom liquid from the second reactive distillation column fed into the high boiling point material separating column A varies depending on the amount of the high-purity diphenyl carbonate to be produced, the concentration of the diphenyl carbonate in the reaction mixture, the separation conditions for the separating column A, and so on, but 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 high boiling point reaction mixture from the second reactive distillation column fed continuously into the high boiling point material separating column A is separated into a column top component (A_T) containing most of the diphenyl carbonate and most of compounds having a lower boiling point than the diphenyl carbonate such as unreacted starting material, an alkyl phenyl ether and the alkyl phenyl carbonate, and a column bottom component (A_B) containing the catalyst, high boiling point by-products and a small amount of the diphenyl carbonate. The column bottom component (A_B) may contain a small amount of the alkyl phenyl carbonate. Such organic material in the column bottom component plays a useful role in dissolving the catalyst component and thus maintaining a liquid state. All or some of the column bottom component (A_B) is generally reused by being circulated back into the first reactive distillation column and / or the second reactive distillation column of step (II) as is as a transesterification reaction

catalyst component, but in some cases the catalyst may be recycled after being separated from the organic matter in a catalyst recovery process, and then reused by being circulated back into the first reactive distillation column and / or the second reactive distillation column of step (I).

It is a characteristic feature of step (II) that in step (II) the catalyst component and by-products having a higher boiling point than the diphenyl carbonate such as phenyl salicylate, xanthone, phenyl methoxybenzoate and 1-phenoxy-carbonyl-2-phenoxy-carboxy-phenylene are almost completely separated off as the column bottom component (A_B) in the high boiling point material separating column A, it being easy to make the content thereof in the column top component (A_T) be generally not more than 200 ppm, preferably not more than 100 ppm, more preferably not more than 50 ppm. It is another characteristic feature of step (II) that despite making the column top component (A_T) hardly contain any such high boiling point by-products, most of the diphenyl carbonate in the reaction mixture introduced into the high boiling point material separating column A can be withdrawn from the top of the column. In step (II), not less than 95%, preferably not less than 96%, more preferably not less than 98%, of the diphenyl 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 step (II), although dependent on the composition of the high boiling point reaction mixture from the second reactive distillation column fed into the separating column A, in general 90 to 97 w% of the liquid continuously fed in is continuously withdrawn from the top of the column as the column top component (A_T), with 10 to 3 w% 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 1 % by weight of the dialkyl carbonate, 1 to 10 % by weight of the phenol, 0.05 to 0.5 % by weight of an alkyl phenyl ether, 20 to 40 % by weight of the alkyl phenyl carbonate, and 50 to 80 % by weight of the diphenyl 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.

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

As stated above, the amount of the column top component (A_T) continuously withdrawn from the top of the high boiling point material separating column A is generally approximately from 90 to 97% of the high boiling point reaction mixture from the second reactive distillation column fed into the separating column A. This column top component (A_T) is continuously fed as is into the diphenyl carbonate purifying column B from the inlet B1 provided at a middle stage 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 diphenyl 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 diphenyl carbonate is contained in the column top component (B_T), this amount generally being from 1 to 9%, preferably from 3 to 8%, based on the diphenyl carbonate fed in. The diphenyl carbonate in the column top component (B_T) is separated out and thus recovered using another distillation column for separating the column top component (B_T). Alternatively, a method in which this diphenyl carbonate is separated off as the column bottom component from this other distillation column, and is then recovered by being returned into the high boiling point material separating column A and / or the diphenyl carbonate purifying column B is also preferable. The column bottom component (B_B) contains the diphenyl carbonate, and a small amount of high boiling point by-products concentrated to approximately a few percent. Another characteristic feature of step (II) is that the amount of the diphenyl 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%, based on the diphenyl carbonate fed in.

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

The purity of the diphenyl carbonate obtained as the side cut component (B_S) in step (II) is generally not less than 99.9%, preferably not less than 99.99%, more preferably not less than 99.999%. The contents of high boiling point impurities in the high-purity diphenyl

carbonate obtained when carrying out step (I) and step (II) with dimethyl carbonate and phenol as the starting material are not more than 30 ppm, preferably not more than 10 ppm, more preferably not more than 1 ppm for phenyl salicylate, 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, 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. 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, the starting material and catalyst not containing a halogen are generally used, and hence the halogen content of the diphenyl carbonate obtained is not more than 0.1 ppm, preferably not more than 10 ppb, more preferably not more than 1 ppb (outside the detection limit for the ion chromatography).

In step (II), the reflux ratio for the diphenyl carbonate purifying column B is in a range of from 0.01 to 10, preferably from 0.1 to 8, more preferably from 0.5 to 5.

The material constituting the high boiling point material separating column A, the diphenyl carbonate purifying column B, 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 diphenyl carbonate produced, stainless steel is preferable.

Next, step (III) is carried out. This is a step of reacting an

aromatic dihydroxy compound and the high-purity diphenyl carbonate together so as to produce an aromatic polycarbonate molten prepolymer, and producing an aromatic polycarbonate using a guide-contacting downflow type polymerization apparatus in which the molten prepolymer is made to flow down along surfaces of guides, and the molten prepolymer is polymerized while flowing down.

The aromatic dihydroxy compound used in step (III) is a compound represented by the following general formula (39);



In formula (39), Ar represents a bivalent aromatic group.

The bivalent aromatic group Ar is preferably, for example, one represented by the following general formula (40);

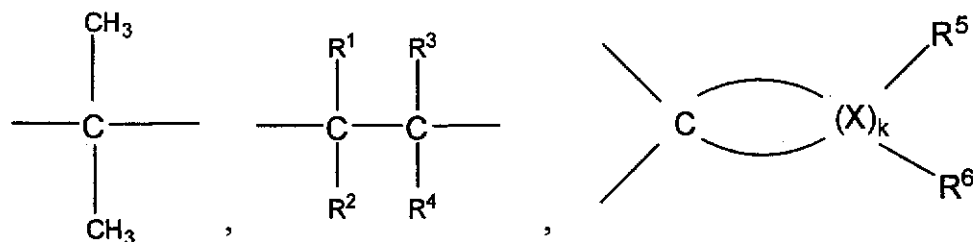


wherein each of Ar^1 and Ar^2 independently represents a bivalent carbocyclic or heterocyclic aromatic group having 5 to 70 carbon atoms, and Y represents a bivalent alkylene group having 1 to 30 carbon atoms.

In each of the bivalent aromatic groups Ar^1 and Ar^2 , one or a plurality of the hydrogen atoms may be substituted with another substituent that does not have an adverse effect on the reaction, for example a halogen atom, an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, a phenyl group, a phenoxy group, a vinyl group, a cyano group, an ester group, an amide group, a nitro group, or the like. A preferable specific example of a heterocyclic aromatic group is an aromatic group having one or a plurality of ring-forming nitrogen atom(s), oxygen atom(s), and / or sulfur atom(s). Each of the bivalent aromatic groups Ar^1 and Ar^2 may represent, for

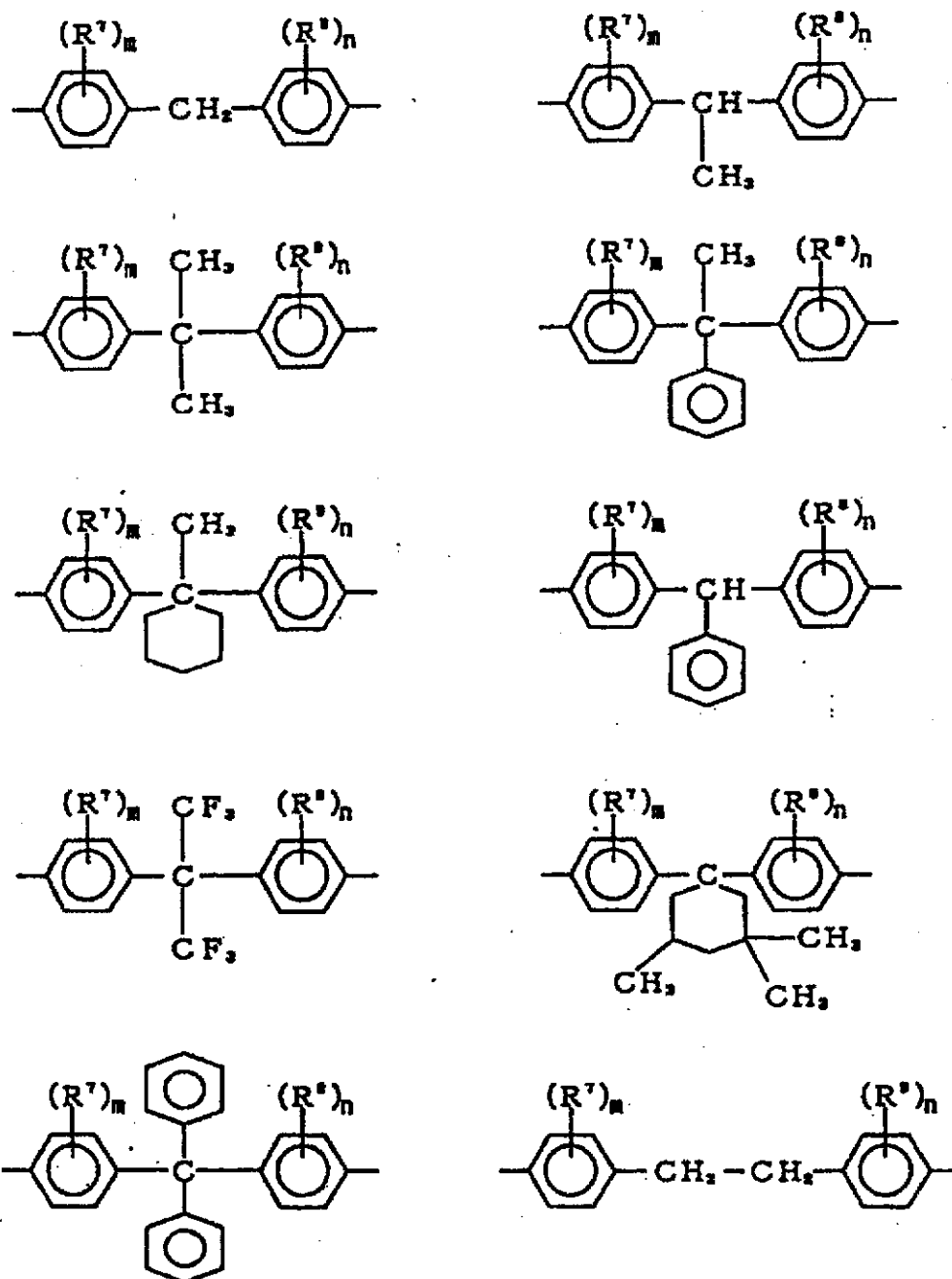
example, a group such as optionally substituted phenylene, optionally substituted biphenylene, or optionally substituted pyridylene. Here, substituents are defined above.

The bivalent alkylene group Y is, for example, an organic group represented by following formula:



wherein each of R¹, R², R³, and R⁴ independently represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, a cycloalkyl group having 5 to 10 carbon atoms in the ring thereof, a carbocyclic aromatic group having 5 to 10 carbon atoms in the ring thereof, or a carbocyclic aralkyl group having 6 to 10 carbon atoms. k represents an integer from 3 to 11, R⁵ and R⁶ are selected separately for each X, each independently representing a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, and each X represents a carbon atom. Moreover, in each of R¹, R², R³, R⁴, R⁵, and R⁶, one or more of the hydrogen atoms may be substituted with another substituent that does not have an adverse effect on the reaction, for example a halogen atom, an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, a phenyl group, a phenoxy group, a vinyl group, a cyano group, an ester group, an amide group, a nitro group, or the like.

Examples of such a bivalent aromatic group Ar are shown in following formula:



wherein each of R^7 and R^8 independently represents a hydrogen atom, a halogen atom, an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, a cycloalkyl group having 5 to 10 carbon atoms in the ring thereof, or a phenyl group, and each of m and n is an integer from 1 to 4; in the case that m is in a range of from 2 to 4, the R^7 's may be the same as or different to one another, and in the case

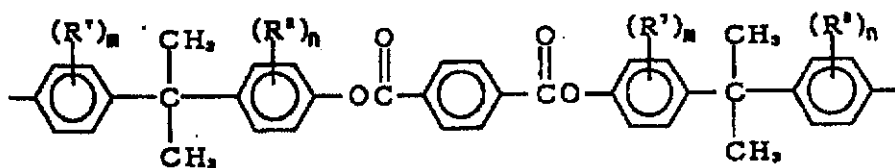
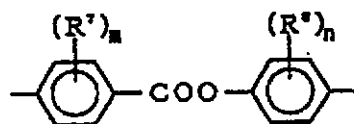
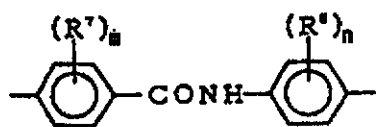
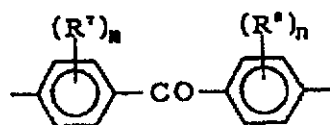
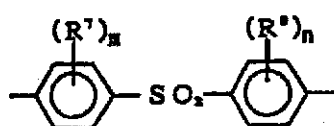
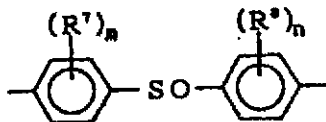
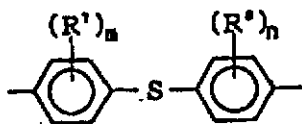
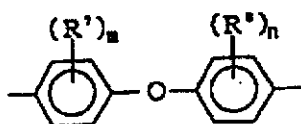
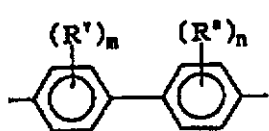
that n is in a range of from 2 to 4, the R^8 's may be the same as or different to one another.

Furthermore, the bivalent aromatic group Ar may be one represented by the following formula;



wherein Ar^1 and Ar^2 are defined above, and Z is a single bond or a bivalent group such as $-\text{O}-$, $-\text{CO}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{SO}-$, $-\text{COO}-$, or $-\text{CON}(\text{R}^1)-$, wherein R^1 is defined above.

Examples of such a bivalent aromatic group Ar are shown in following formula;



wherein R^7 , R^8 , m and n are defined above.

Furthermore, specific examples of the bivalent aromatic group Ar include unsubstituted or substituted phenylene, unsubstituted or substituted naphthylene, and unsubstituted or substituted pyridylene.

In the present invention, one such aromatic dihydroxy compound may be used, or a plurality may be used. A typical example of the aromatic dihydroxy compound is bisphenol A. Moreover, in the present invention, the aromatic dihydroxy compound may be used together with an aromatic trihydroxy compound for introducing a branched structure so long as this is within a range such as not to impair the object of the present invention.

The ratio between the aromatic dihydroxy compound and the high-purity diphenyl carbonate used in step (III) varies depending on the type of the aromatic dihydroxy compound and the diphenyl carbonate used, and the polymerization temperature and other polymerization conditions, but the diphenyl carbonate is generally used in a proportion in a range of from 0.9 to 2.5 mol, preferably from 0.95 to 2.0 mol, more preferably from 0.98 to 1.5 mol, based on 1 mol of the aromatic dihydroxy compound.

The prepolymer in a molten state (hereinafter referred to as the "molten prepolymer") produced from the aromatic dihydroxy compound and the diphenyl carbonate in step (III) means partially polymerized molten material produced from the aromatic dihydroxy compound and the diphenyl carbonate having a lower polymerization degree than the aromatic polycarbonate having the desired polymerization degree, and may of course be an oligomer. The molten prepolymer used in step (III)

may be obtained through any publicly known process. For example, the molten prepolymer can be produced by stirring a molten mixture containing predetermined amounts of the aromatic dihydroxy compound and the diphenyl carbonate under normal pressure and / or a reduced pressure at a temperature in a range of from approximately 120 °C to approximately 280 °C using one or a plurality of vertical stirring tank(s), while removing phenol by-produced through the reaction. A process in which a plurality of vertical stirring tanks linked together in series are used, and the polymerization degree is progressively increased so as to continuously produce a molten prepolymer having a required polymerization degree is particularly preferable.

In step (III), the molten prepolymer is continuously fed into a guide-contacting downflow type polymerization apparatus, so as to continuously produce an aromatic polycarbonate having a desired polymerization degree. The guide-contacting downflow type polymerization apparatus is a polymerization apparatus in which the prepolymer is subjected to polymerization while being made to flow down in a molten state along guides, and is such that not less than 1 ton / hr of the aromatic polycarbonate can be produced. The guide-contacting downflow type polymerization apparatus must be:

(1) an apparatus of a type having a molten prepolymer receiving port, a perforated plate, a polymerization reaction zone having a plurality of guides that extend downward from the perforated plate provided in a space surrounded by the perforated plate, a side casing and a tapered bottom casing, a molten prepolymer feeding zone for feeding the molten prepolymer via the perforated plate onto the guides in the polymerization

reaction zone, a vacuum vent provided in the polymerization reaction zone, an aromatic polycarbonate discharge port provided in a lowermost portion of the tapered bottom casing, and an aromatic polycarbonate discharge pump connected to the discharge port, wherein:

(2) an internal sectional area A (m^2) taken through a horizontal plane of the side casing in the polymerization reaction zone satisfies the formula (22);

$$0.7 \leq A \leq 300 \quad (22),$$

(3) a ratio between A (m^2) and an internal sectional area B (m^2) taken through a horizontal plane of the aromatic polycarbonate discharge port satisfies the formula (23);

$$20 \leq A / B \leq 1000 \quad (23),$$

(4) the tapered bottom casing in the polymerization reaction zone is connected at an internal angle C ($^\circ$) to the side casing thereabove, wherein the angle C ($^\circ$) satisfies the formula (24),

$$120 \leq C \leq 165 \quad (24),$$

(5) a length h (cm) of each of the guides satisfies the formula (25),

$$150 \leq h \leq 5000 \quad (25), \text{ and}$$

(6) a total external surface area S (m^2) of the guides satisfies the formula (26),

$$2 \leq S \leq 50000 \quad (26).$$

To produce a high-quality high-performance aromatic polycarbonate stably for a prolonged period of time with no variation in molecular weight in an amount on an industrial scale of not less than 1 ton/hr, a polymerization apparatus satisfying various conditions is required; in the present invention, these conditions have been discovered.

Note that in the present invention, "no variation in molecular weight" means that the variation in the number average molecular weight is not more than 200. In the present invention, the aromatic polycarbonate can be produced stably for a prolonged period of time with variation in the number average molecular weight being preferably not more than 150, more preferably not more than 100.

More specifically, the internal sectional area A (m^2) taken through a horizontal plane (plane a-a') of side casing 10 in polymerization reaction zone 5 as shown in the schematic view of FIG. 4 must satisfy the above formula (22).

If A is less than $0.7 m^2$, then the desired production amount cannot be attained. Moreover, to attain such a production amount while keeping down the equipment cost, A must be made to be not more than $300 m^2$.

Furthermore, the ratio between A (m^2) and the internal sectional area B (m^2) taken through a horizontal plane (plane b-b') of aromatic polycarbonate discharge port 7 must satisfy the above formula (23).

A / B must satisfy the above formula (23) so that the molten material of high melt viscosity containing the produced aromatic polycarbonate or aromatic polycarbonate prepolymer of increased polymerization degree can be discharged without causing a drop in the quality of this molten matter.

Furthermore, the tapered bottom casing 11 in polymerization reaction zone 5 is provided at an internal angle C ($^\circ$) to the side casing 10 thereabove, wherein the angle C ($^\circ$) must satisfy the above formula (24). To keep down the equipment cost, C is preferably as close as

possible to 90°, but to move the molten material of high melt viscosity containing the aromatic polycarbonate or aromatic polycarbonate prepolymer of increased polymerization degree falling down from the lower ends of guides 4 to the discharge port 7 without bringing about a reduction in the quality of this molten matter, C must satisfy the above formula (24).

Furthermore, the length h (cm) of each of the guides 4 must satisfy the above formula (25). It is undesirable for h to be shorter than 150 cm, since then the polymerization degree of the molten prepolymer cannot be increased sufficiently, and moreover the variation in the polymerization degree may become greater than approximately 200 in terms of the number average molecular weight. It is undesirable for h to be longer than 5000 cm, since then the difference in the melt viscosity of the molten prepolymer between the top and the bottom of each guide becomes too great, and hence the variation in the polymerization degree becomes greater than approximately 300 (in some cases greater than approximately 500) in terms of the number average molecular weight, and hence variation arises in the properties of the aromatic polycarbonate obtained. Note that the variation in the polymerization degree being great in the present invention means, for example, the case of variation such that there is a difference of more than approximately 200 in terms of the number average molecular weight.

Furthermore, the total external surface area S (m^2) of the guides 4 must satisfy the above formula (26). If S is less than $2 m^2$, then the desired production amount cannot be attained. Moreover, to attain such a production amount while keeping down the equipment cost, and to

eliminate variation in properties, S must be made to be not more than 50000 m².

It has been discovered that by using a guide-contacting downflow type polymerization apparatus simultaneously satisfying the formulae (22), (23), (24), (25) and (26), surprisingly, a high-quality and high-performance aromatic polycarbonate having excellent mechanical properties and no discoloration can be produced in an amount of not less than 1 ton / hr for a prolonged period of time of not less than several thousand hours, for example not less than 5,000 hours, stably with no variation in the molecular weight. In the case that these conditions are not simultaneously satisfied, problems occur such as the desired production amount not being obtained, a variation in the number average molecular weight of more than approximately 200 arising, stable production not being possible for 1,000 hours, or discoloration being prone to occur.

The reason why it has become possible to produce the aromatic polycarbonate on an industrial scale with such excellent effects in step (III) is not clear, but this is supposed to be that, in addition to the reasons described above, a composite effect arises when the above conditions are combined. For example, it is supposed that this is because if the guides having a high surface area satisfying the formulae (25) and (26) are used, then the molten prepolymer can be polymerized at a relatively low temperature, and a large amount of high-quality aromatic polycarbonate having a desired molecular weight can be produced; moreover, the tapered bottom casing satisfying the formula (24) makes it possible to shorten the time taken for the large amount of

the produced high-quality aromatic polycarbonate falling down from the guides to reach the discharge port, whereby the heat history of the produced aromatic polycarbonate can be reduced.

Note that this art for production on an industrial scale can only be established through prolonged operation using large-scale production equipment, and it goes without saying that the cost of the production equipment here is an important factor that must be taken into consideration. Another effect of the present invention is that the equipment cost of the industrial production equipment can be reduced by using the guide-contacting downflow type polymerization apparatus satisfying the formulae (22), (23), (24), (25) and (26).

Ranges required for dimensions, angles and so on for the guide-contacting downflow type polymerization apparatus used in step (III) have been described above, but more preferable ranges are as follows. A more preferable range for the internal sectional area A (m^2) taken through a horizontal plane of the side casing in the polymerization reaction zone is $0.8 \leq A \leq 250$, with $1 \leq A \leq 200$ being yet more preferable.

Moreover, a more preferable range for the ratio between A (m^2) and the internal sectional area B (m^2) taken through a horizontal plane of the aromatic polycarbonate discharge port is $25 \leq A / B \leq 900$, with $30 \leq A / B \leq 800$ being yet more preferable.

Moreover, a more preferable range for the internal angle C ($^\circ$) of the tapered bottom casing in the polymerization reaction zone to the side casing thereabove is $125 \leq C \leq 160$, with $135 \leq C \leq 165$ being yet more preferable. Note that in the case of progressively increasing the

polymerization degree using a plurality of guide-contacting downflow type polymerization apparatuses, taking the angles for the guide-contacting downflow type polymerization apparatuses to be $C_1, C_2, C_3 \dots$ respectively, it is preferable to make $C_1 \leq C_2 \leq C_3 \leq \dots$

Moreover, the required length h (cm) of each of the guides varies with factors such as the polymerization degree of the starting material prepolymer, the polymerization temperature and pressure, and the polymerization degree and amount of the aromatic polycarbonate or prepolymer to be produced using the polymerization apparatus, but generally a more preferable range is $200 \leq h \leq 3000$, with $250 \leq h \leq 2500$ being yet more preferable. It is particularly preferable for h to satisfy the formula (33);

$$400 < h \leq 2500 \quad (33).$$

Moreover, the required total external surface area S (m^2) of the guides also varies with factors such as the above, but generally a more preferable range is $4 \leq S \leq 40000$, with $10 \leq S \leq 30000$ being yet more preferable. A particularly preferable range is $15 \leq S \leq 20000$. In the present invention, the "total external surface area of the guides" means the total surface area of the guides with which the molten prepolymer contacts when flowing down; for example, in the case of a guide such as a pipe, this means the surface area of the outside of the pipe, the surface area of the surface inside the pipe over which the molten prepolymer does not flow down not being included.

In the guide-contacting downflow type polymerization apparatus used in step (III), the shape of the inside section taken through a horizontal plane of the side casing in the polymerization reaction zone

may be any shape, for example polygonal, elliptical or circular.

Operation is generally carried out with the polymerization reaction zone under a reduced pressure, and hence any shape is acceptable so long as this reduced pressure can be withstood, but a circular shape or a shape close thereto is preferable. The side casing in the polymerization reaction zone in the present invention is thus preferably cylindrical. In this case, it is preferable for the tapered conical bottom casing to be connected to a lower portion of the cylindrical side casing, with a cylindrical aromatic polycarbonate discharge port being provided in the lowermost portion of this bottom casing. Taking the cylindrical portion of the side casing to have an inside diameter D (cm) and a length L (cm), and taking the discharge port to have an inside diameter d (cm), D , L and d preferably satisfy the following formulae (29), (30), (31) and (32);

$$100 \leq D \leq 1800 \quad (29)$$

$$5 \leq D / d \leq 50 \quad (30)$$

$$0.5 \leq L / D \leq 30 \quad (31) \text{ and}$$

$$h - 20 \leq L \leq h + 300 \quad (32),$$

For the guide-contacting downflow type polymerization apparatus, a more preferable range for D (cm) is $150 \leq D \leq 1500$, with $200 \leq D \leq 1200$ being yet more preferable. Moreover, a more preferable range for D / d is $6 \leq D / d \leq 45$, with $7 \leq D / d \leq 40$ being yet more preferable. Moreover, a more preferable range for L / D is $0.6 \leq L / D \leq 25$, with $0.7 \leq L / D \leq 20$ being yet more preferable. Moreover, a more preferable range for L (cm) is $h - 10 \leq L \leq h + 250$, with $h \leq L \leq h + 200$ being yet more preferable.

The precise reason why the high-quality and high-performance

aromatic polycarbonate having excellent mechanical properties with no discoloration can be produced stably with no variation in molecular weight for a prolonged period of time on an industrial scale with a fast polymerization rate in step (III) is not clear, but is thought to be as follows. That is, according to the guide-contacting downflow type polymerization process used in step (III), the starting material molten prepolymer is led from the receiving port 1 via the feeding zone 3 and the perforated plate 2 to the guides 4, and then has the polymerization degree thereof increased while flowing down along the guides. Effective internal stirring and surface renewal of the molten prepolymer are carried out as the molten prepolymer flows down along the guides, and thus removal of phenol or the like is carried out effectively, whereby the polymerization proceeds at a fast rate. The melt viscosity increases as the polymerization proceeds, and hence the adhesion force of the flowing down melt material to the guides increases, and thus the amount of the molten material stuck to each guide increases toward the bottom of the guide. This means that the residence time of the molten prepolymer on the guide, i.e. the polymerization reaction time, increases. Moreover, for the molten prepolymer, which flows down under its own weight while being supported on the guide, the surface area per unit weight is very high, and hence surface renewal is carried out efficiently. Increase of molecular weight in the latter half of polymerization, which has been impossible with prior mechanical stirring type polymerization apparatuses, can thus be attained easily. This is one of the excellent characteristic features of the polymerization apparatus used in step (III).

The only reason that the amount of the molten material stuck to

the guides increases in the latter half of the polymerization below a middle portion of each of the guides is the adhesive holding force, which corresponds to the melt viscosity, and hence approximately the same amount of the molten material having approximately the same melt viscosity is supported at the same height on each of the guides. Meanwhile, the molten material is continuously fed onto the guides from the top thereof, and hence molten material of increased polymerization degree having approximately the same melt viscosity continuously falls down into the bottom portion of the casing from the lower ends of the guides. That is, aromatic polycarbonate of approximately the same polymerization degree produced while flowing down the guides collects in the tapered bottom portion of the casing, and hence aromatic polycarbonate with no variation in molecular weight can be continuously produced. This is another excellent characteristic feature of the polymerization apparatus used in the present invention. The aromatic polycarbonate collected in the tapered bottom portion of the casing is continuously withdrawn through the discharge port 7 by a discharging pump 8, and is then generally continuously pelletized via an extruder. In this case, additives such as a stabilizer and a weatherproofing agent may be added in the extruder.

The perforated plate in the guide-contacting downflow type polymerization apparatus used in step (III) is generally selected from flat plates, corrugated plates, and plates that are thickened in a middle portion thereof; the shape of the perforated plate is generally selected from shapes such as circular, oval, triangular, and polygonal. The shape of each of the holes in the perforated plate is generally selected

from shapes such as circular, oval, triangular, slit-shaped, polygonal, and star-shaped. The sectional area of each of the holes is generally in a range of from 0.01 to 100 cm², preferably from 0.05 to 10 cm², particularly preferably from 0.1 to 5 cm². The spacing between holes, specifically the distance between hole centers, is generally in a range of from 1 to 500 mm, preferably from 25 to 100 mm. The holes in the perforated plate may be holes that penetrate through the perforated plate, or alternatively pipes may be installed in the perforated plate. Moreover, the holes may be tapered.

The "guides" in the guide-contacting downflow type polymerization apparatus used in step (III) indicate members for each of which the ratio of the length in a direction perpendicular to a horizontal section relative to the average length of the outer periphery of this horizontal section is very high. This ratio is generally in a range of from 10 to 1,000,000, preferably from 50 to 100,000. The shape of the horizontal section is generally selected from shapes such as circular, oval, triangular, square, polygonal, and star-shaped. The shape of this section may be constant, or may vary, in the length direction. Moreover, each of the guides may be hollow.

Each of the guides may be a single wire, a single thin rod, a single thin pipe made to be such that the molten prepolymer cannot enter therein, or the like, or a plurality of such guides may be combined using a method such as twisting together. Moreover, the guides may form a mesh-like structure, or a punching plate-like structure. The surface of each guide may be smooth, or may be uneven, and may have projections or the like in places. Preferable guides are cylindrical ones such as

wires or thin rods, thin pipes as described above, mesh-like guide structures, and punching plate-like guide structures.

The guides may themselves have a heating source such as a heating medium or an electrical heater therein, but guides not having such a heating source therein are particularly preferable since then there is no risk of thermal deterioration of the prepolymer or aromatic polycarbonate on the surface of the guides.

In the guide-contacting downflow type polymerization apparatus used in the present invention, which enables production of the high-quality aromatic polycarbonate on the industrial scale (in terms of production amount, prolonged stable production, etc.), a particularly preferable guide structure is one of a type in which a plurality of guides each having the form of a wire or a thin rod or a thin pipe as described above are joined together at suitable vertical intervals using transverse supports from the top to the bottom of the guides. Examples are mesh-like guide structures in which a plurality of guides each having the form of a wire or a thin rod or a thin pipe as described above are fixed together using transverse supports from the top to the bottom of the guides at suitable vertical intervals, for example intervals in a range of from 1 to 200 cm, a three-dimensional guide structure in which a plurality of such mesh-like guide structures are arranged in front of and behind one another and joined together using transverse supports at suitable vertical intervals, for example intervals in a range of from 1 to 200 cm, or a jungle-gym-like three-dimensional guide structure in which a plurality of guides each having the form of a wire or a thin rod or a thin pipe as described above are fixed together in front of and behind, and left and

right of, one another using transverse supports at suitable vertical intervals, for example intervals in a range of from 1 to 200 cm. The transverse supports are not only useful for keeping the intervals between the guides approximately constant, but are also useful for increasing the overall strength of flat or curved guides, or guides forming a three-dimensional structure. The supports may be of the same material as the guides, or a different material.

For the guide-contacting downflow type polymerization apparatus, in the case that each guide is cylindrical, or has the form of a pipe made to be such that the molten prepolymer cannot enter therein, with an outside diameter r (cm), r preferably satisfies the following formula (34);

$$0.1 \leq r \leq 1 \quad (34).$$

The guides promote polymerization of the molten prepolymer as the molten prepolymer flows down the guides, and also have a function of holding the molten prepolymer for a certain period of time. This holding time is related to the polymerization reaction time. As described above, as the polymerization proceeds, the melt viscosity of the molten prepolymer progressively increases, and hence the holding time and the amount held progressively increase. For a given melt viscosity, the amount of the molten prepolymer held by the guides varies with the external surface area of the guides, i.e. in the case of cylindrical or pipe-shaped guides, with the outside diameter.

Moreover, the guides installed in the polymerization apparatus used in the present invention must be strong enough to support their own weight plus the weight of the molten prepolymer being held. For this reason, the thickness of the guides is important, and in the case of

cylindrical or pipe-shaped guides, the formula (34) is preferably satisfied. If r is less than 0.1, then prolonged stable operation becomes difficult in terms of the strength, whereas if r is greater than 1, then the guides themselves become very heavy, and hence there are problems such as having to make the perforated plate very thick so as to hold the guides in the polymerization apparatus, and moreover there is an increase in parts where the amount of the molten prepolymer held is too high, resulting in problems such as variation in the molecular weight increasing. For such reasons, a more preferable range for r is $0.15 \leq r \leq 0.8$, with $0.2 \leq r \leq 0.6$ being yet more preferable.

A preferable material for the guides is one selected from metals such as stainless steel, carbon steel, hastelloy, nickel, titanium, chromium, aluminum, and other alloys, highly heat-resistant polymeric materials, and so on. Stainless steel is particularly preferable. Moreover, surfaces of the guides may be subjected to any of various treatments as necessary such as plating, lining, passivation treatment, acid washing, or washing with phenol.

There are no particular limitations on the positional relationship between the guides and the perforated plate or the positional relationship between the guides and the holes in the perforated plate so long as the molten prepolymer can contact and flow down the guides. The guides and the perforated plate may be in contact with one another, or not in contact with one another. Although there is no such limitation, it is preferable to install the guides in correspondence with the holes in the perforated plate. The reason for this is that design may then be carried out such that the molten prepolymer falling down from the perforated

plate contacts the guides in suitable positions. Specific preferable examples of installing the guides in correspondence with the holes in the perforated plate include: (1) a method in which the upper end of each guide is fixed to an upper inner wall of the polymerization apparatus, and the guides are provided such that each guide penetrates through the vicinity of a nearly central portion of a hole in the perforated plate; (2) a method in which the upper end of each guide is fixed to a peripheral portion at an upper end of a hole in the perforated plate, and the guides are provided such that each guide penetrates through a hole in the perforated plate; and (3) a method in which the upper end of each guide is fixed to the underside of the perforated plate.

Examples of methods for making the molten prepolymer pass through the perforated plate and flow down along the guides are a method in which the molten prepolymer is allowed to flow down through its own weight or the liquid head, and a method in which the molten prepolymer has pressure applied thereto using a pump or the like and is thus extruded from the perforated plate. A preferable method is one in which a predetermined amount of the starting material molten prepolymer is fed into the feeding zone of the polymerization apparatus under pressure using a feed pump, and then the molten prepolymer thus led onto the guides via the perforated plate flows down along the guides under its own weight. The molten prepolymer is generally continuously fed into the guide-contacting downflow type polymerization apparatus after having been heated to a predetermined polymerization temperature. It is thus generally preferable for a jacket or the like to be installed on an outer wall of the guide-contacting downflow type polymerization

apparatus, and to carry out heating to a predetermined temperature by passing a heating medium or the like through the jacket, thus heating or maintaining the temperature of the molten prepolymer, the prepolymer feeding zone and the perforated plate, and maintaining the temperature of the polymerization reaction zone, the side casing and the tapered bottom casing.

In step (III), the temperature of the reaction in which the molten prepolymer obtained from the aromatic dihydroxy compound and the diphenyl carbonate is subjected to the polymerization in the guide-contacting downflow type polymerization apparatus so as to produce the aromatic polycarbonate is generally in a range of from 80 to 350 °C. However, according to the polymerization apparatus used in the present invention, efficient surface renewal is carried out accompanying internal stirring, and hence the polymerization reaction can be made to proceed at a relatively low temperature. A preferable reaction temperature is thus in a range of from 100 to 290°C, more preferably from 150 to 270°C. With a horizontal biaxial stirring type reaction for ultra-high viscosity polymer, which reactor is a conventional polymerization apparatus, it has generally been necessary to stir for a prolonged period of time at a high temperature of not less than 300 °C under a high vacuum of not more than 133 Pa. Moreover, it has not been possible to avoid yellowing due to leaking in of air, and ingress of foreign matter, through a stirring shaft seal. However, with the polymerization apparatus used in the present invention, because there is no mechanical stirring, there is no such stirrer seal, and hence there is very little leaking in of air and so on. Furthermore, another

characteristic feature of the present invention is that the polymerization can be carried out adequately at a temperature lower by approximately 20 to 50 °C than in the case of the conventional horizontal biaxial stirring type reactor for ultra-high viscosity polymer. This is another big factor in it being possible to produce the high-quality aromatic polycarbonate with no discoloration or deterioration in properties in the present invention.

Moreover, even if the conventional horizontal biaxial stirring type reactor for ultra-high viscosity polymer is used, producing an aromatic polycarbonate of medium viscosity grade or above is impossible due to the ultra-high viscosity of the aromatic polycarbonate, but with the guide-contacting downflow type polymerization apparatus used in the present invention, even a high viscosity grade aromatic polycarbonate can be produced easily. That is, with the guide-contacting downflow type polymerization apparatus used in the present invention, aromatic polycarbonates of all grades from a disk grade having a relatively low molecular weight up to a high viscosity grade can be produced. This is also a big characteristic feature of the present invention.

In step (III), as the polymerization reaction proceeds, phenol is produced, but this is removed from the reaction system, whereby the reaction rate can be increased. A method in which an inert gas that does not have an adverse effect on the reaction such as nitrogen, argon, helium, carbon dioxide or a lower hydrocarbon gas is introduced into the polymerization apparatus, and the phenol produced is entrained by this gas and thus removed, a method in which the reaction is carried out under a reduced pressure, or the like is thus preferably used.

Alternatively, a method in which these two methods are used together can also be preferably used. In such a case, there is no need to introduce a large amount of the inert gas into the polymerization apparatus, but rather just enough to maintain an inert gas atmosphere inside the apparatus is sufficient.

Furthermore, a method in which the inert gas is absorbed into the molten prepolymer in advance before the molten prepolymer is fed into the guide-contacting downflow type polymerization apparatus, and then the molten prepolymer having the inert gas absorbed therein is subjected to the polymerization is also preferable.

A preferable reaction pressure in the polymerization apparatus in step (III) varies depending on the type and molecular weight of the aromatic polycarbonate to be produced, the polymerization temperature, and so on, but in the case, for example, of producing an aromatic polycarbonate from the molten prepolymer produced from bisphenol A and diphenyl carbonate, in the case of a number average molecular weight of less than 5,000, the reaction pressure is preferably in a range of from 400 to 3,000 Pa, and in the case of a number average molecular weight in a range of from 5,000 to 10,000, the reaction pressure is preferably in a range of from 50 to 500 Pa. In the case of a number average molecular weight greater than 10,000, the reaction pressure is preferably less than 300 Pa, particularly preferably in a range of from 20 to 250 Pa.

When carrying out step (III), the aromatic polycarbonate having the desired polymerization degree can be produced using only one such guide-contacting downflow type polymerization apparatus, but depending

on the polymerization degree of the molten prepolymer used as the starting material, the produced amount of the aromatic polycarbonate, and so on, a system in which a plurality of such guide-contacting downflow type polymerization apparatuses are linked together so that the polymerization degree is progressively increased may be preferable. In this case, guides and reaction conditions suitable for the polymerization degree of the prepolymer or aromatic polycarbonate to be produced are preferably adopted for each of the polymerization apparatuses individually. For example, in the case of a system in which a first guide-contacting downflow type polymerization apparatus, a second guide-contacting downflow type polymerization apparatus, a third guide-contacting downflow type polymerization apparatus, a fourth guide-contacting downflow type polymerization apparatus ... are used so that the polymerization degree is progressively increased, taking the total external surface areas of the guides possessed by the polymerization apparatuses to be S_1 , S_2 , S_3 , S_4 ... respectively, the system can be made to be such that $S_1 \geq S_2 \geq S_3 \geq S_4 \geq \dots$.

Moreover, the polymerization temperature may be the same in each of the polymerization apparatuses, or alternatively may be progressively increased. Furthermore, the polymerization pressure may be progressively reduced in the polymerization apparatuses. In this sense, in the case, for example, of progressively increasing the polymerization degree using two polymerization apparatuses, i.e. the first guide-contacting downflow type polymerization apparatus and the second guide-contacting downflow type polymerization apparatus, it is preferable to use guides such that the total external surface area S_1 (m^2) of the

guides in the first polymerization apparatus and the total external surface area S_2 (m^2) of the guides in the second guide-contacting downflow type polymerization apparatus satisfy the following formula (35);

$$1 \leq S_1 / S_2 \leq 20 \quad (35).$$

If S_1 / S_2 is less than 1, then problems arise such as variation in the molecular weight increasing so that prolonged stable production becomes difficult, and it becomes difficult to obtain a predetermined production amount, whereas if S_1 / S_2 is greater than 20, then the flow rate of the molten prepolymer flowing down the guides in the second polymerization apparatus becomes high, and as a result problems arise such as the residence time of the molten prepolymer becoming short so that it becomes difficult to obtain the aromatic polycarbonate of the required molecular weight. For such reasons, a more preferable range is $1.5 \leq S_1 / S_2 \leq 15$.

In step (III), not less than 1 ton / hr of the aromatic polycarbonate is produced; but because the phenol by-produced in the polymerization reaction is discharged out of the system, the molten prepolymer must be fed into the polymerization apparatus in an amount greater than 1 ton / hr. The amount of the molten prepolymer fed into the polymerization apparatus thus varies depending on the polymerization degree thereof and the polymerization degree of the aromatic polycarbonate to be produced, but is generally in a range of from 1.01 to 1.5 ton / hr per 1 ton / hr of the aromatic polycarbonate to be produced.

The reaction in which the aromatic polycarbonate is produced from the aromatic dihydroxy compound and the diphenyl carbonate in step (III) can be carried out without adding a catalyst, but may be carried out in

the presence of a catalyst as required so as to increase the polymerization rate. There are no particular limitations on such a catalyst, which may be any used in the field in question. Examples of the catalyst include alkali metal and alkaline earth metal hydroxides such as lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide; alkali metal salts, alkaline earth metal salts and quaternary ammonium salts of boron and aluminum hydrides such as lithium aluminum hydride, sodium borohydride and tetramethylammonium borohydride; alkali metal and alkaline earth metal hydrides such as lithium hydride, sodium hydride and calcium hydride; alkali metal and alkaline earth metal alkoxides such as lithium methoxide, sodium ethoxide and calcium methoxide; alkali metal and alkaline earth metal aryloxides such as lithium phenoxide, sodium phenoxide, magnesium phenoxide, and LiO-Ar-OLi and NaO-Ar-ONa (wherein Ar represents an aryl group); alkali metal and alkaline earth metal organic acid salts such as lithium acetate, calcium acetate and sodium benzoate; zinc compounds such as zinc oxide, zinc acetate and zinc phenoxide; boron compounds such as boron oxide, boric acid, sodium borate, trimethyl borate, tributyl borate, triphenyl borate, and ammonium borates represented by $(\text{R}^1\text{R}^2\text{R}^3\text{R}^4)\text{NB}(\text{R}^1\text{R}^2\text{R}^3\text{R}^4)$ and phosphonium borates represented by $(\text{R}^1\text{R}^2\text{R}^3\text{R}^4)\text{PB}(\text{R}^1\text{R}^2\text{R}^3\text{R}^4)$ (wherein R^1 , R^2 , R^3 and R^4 are defined as above); silicon compounds such as silicon oxide, sodium silicate, tetraalkylsilicon compounds, tetraarylsilicon compounds and diphenyl-ethyl-ethoxysilicon; germanium compounds such as germanium oxide, germanium tetrachloride, germanium ethoxide and germanium phenoxide; tin compounds such as tin oxide, dialkyltin oxides, dialkyltin

carboxylates, tin acetate, tin compounds in which alkoxy groups or aryloxy groups are bonded to tin such as ethyltin tributoxide, and organotin compounds; lead compounds, such as lead oxide, lead acetate, lead carbonate, basic lead carbonate, and lead and organolead alkoxides and aryloxides; onium compounds such as quaternary ammonium salts, quaternary phosphonium salts and quaternary arsonium salts; antimony compounds such as antimony oxide and antimony acetate; manganese compounds such as manganese acetate, manganese carbonate and manganese borate; titanium compounds such as titanium oxide, and titanium alkoxides and titanium aryloxides; and zirconium compounds such as zirconium acetate, zirconium oxide, zirconium alkoxides and aryloxides, and zirconium acetylacetone.

In the case of using such a catalyst, one such catalyst may be used, or a plurality of the catalysts may be used in combination. The amount used of the catalyst is generally selected from a range of from 10^{-10} to 1 % by weight, preferably from 10^{-9} to 10^{-1} % by weight, more preferably from 10^{-8} to 10^{-2} % by weight, based on the starting material aromatic dihydroxy compound. In the case of the melt transesterification method, the polymerization catalyst used remains in the product aromatic polycarbonate, and often has an adverse effect on the polymer properties. It is thus preferable to reduce the amount used of the catalyst as much as possible. According to the process of the present invention, the polymerization can be carried out efficiently, and hence the amount used of the catalyst can be made low. This is one of the characteristic features of the present invention enabling the high-quality aromatic polycarbonate to be produced.

There are no particular limitations on the material of the guide-contacting downflow type polymerization apparatus and conduits used in step (III), but this material is generally selected from metals such as stainless steel, carbon steel, hastelloy, nickel, titanium, chromium, and other alloys, highly heat-resistant polymeric materials, and so on. Moreover, the surface of the material may be subjected to any of various treatments as necessary such as plating, lining, passivation treatment, acid washing, or washing with phenol. Stainless steel, nickel, and a glass lining are particularly preferable.

In step (III), when producing the prepolymer, and during the polymerization in the guide-contacting downflow type polymerization apparatus, a large amount of the phenol by-produced in the reaction is generally continuously withdrawn in a gaseous form, and condensed into a liquid form and thus recovered. In the present invention, a phenol recycling step (IV) of circulating the phenol by-produced in step (III) back into the diphenyl carbonate production step (I) must be carried out. In an industrial production process, recovering all of the by-produced phenol or as much as possible thereof with as little loss as possible, and circulating back and thus reusing this phenol is important. The by-produced phenol by-produced in step (III) and recovered in the present invention generally contains some diphenyl carbonate but still has high purity, and hence can be circulated back into the diphenyl carbonate production step (I) and thus reused as is. In the case that a small amount of aromatic dihydroxy compound or a trace amount of oligomer is contained in the recovered phenol, it is preferable to remove this high boiling point material by further carrying out distillation before

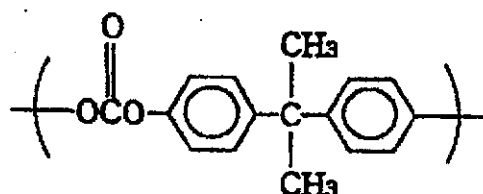
circulating the phenol back into the diphenyl carbonate production step (I) for reuse.

The aromatic polycarbonate produced by implementing the system of the present invention has a repeat unit represented by following formula:



wherein Ar is defined as before.

A particularly preferable aromatic polycarbonate is one containing not less than 85 mol% of the repeat unit represented by following formula out of all the repeat units;



Moreover, terminal groups of the aromatic polycarbonate produced by implementing the process according to the present invention are generally hydroxy groups and / or phenyl carbonate groups (or substituted phenyl carbonate groups).

There are no particular limitations on the ratio of hydroxy groups to phenyl carbonate groups (or substituted phenyl carbonate groups), but this ratio is generally in a range of from 95:5 to 5:95, preferably from 90:10 to 10:90, more preferably from 80:20 to 20:80. An aromatic polycarbonate in which the proportion of phenyl carbonate groups (or substituted phenyl carbonate groups) among the terminal groups is not

less than 60 mol% is particularly preferable.

The aromatic polycarbonate produced by implementing the process according to the present invention may have a main chain thereof partially branched through foreign linkages such as ester linkages or ether linkages. The amount of such foreign linkages is generally in a range of from 0.005 to 2 mol%, preferably from 0.01 to 1 mol%, more preferably from 0.05 to 0.5 mol %, based on the carbonate linkages. Such an amount of foreign linkages is suitable for precision molding since the flow characteristics during melt molding can be improved without other polymer properties being worsened; molding can be carried out even at a relatively low temperature, and a molded article having excellent performance can be produced. The molding cycle can also be shortened, contributing to energy saving during the molding.

The aromatic polycarbonate produced by implementing the process according to the present invention hardly contains any impurities, it being possible to produce an aromatic polycarbonate containing 0.001 to 1 ppm of alkali metal and / or alkaline earth metal compounds in terms of the metallic elements therein. This content is preferably in a range of from 0.005 to 0.5 ppm, more preferably from 0.01 to 0.1 ppm. In the case that the content of such metallic elements is not more than 1 ppm, preferably not more than 0.5 ppm, more preferably 0.1 ppm, there are no adverse effects on the properties of the aromatic polycarbonate product, and hence the aromatic polycarbonate produced through the present invention is of high quality.

The aromatic polycarbonate produced by implementing the process according to the present invention is particularly preferably one

produced using the aromatic dihydroxy compound and the diphenyl carbonate each not containing a halogen, the halogen content generally being not more than 10 ppb. According to the process of the present invention, even an aromatic polycarbonate having a halogen content of not more than 5 ppb, more preferably not more than 1 ppb, can be produced, and hence a product having very high quality can be obtained.

It is clear from the Examples, described below, that in the process according to the present invention, it is because the specified polymerization apparatus is used that the aromatic polycarbonate can be produced stably for a prolonged period of time with no variation in molecular weight.

Examples

Following is a more detailed description of the present invention through Examples. However, the present invention is not limited to the following Examples.

· Number average molecular weight (Mn): Measurement was carried out by a gel permeation chromatography (GPC) method using tetrahydrofuran as a transporting solvent, and the number average molecular weight (Mn) was determined using a converted molecular weight calibration curve given by the following formula obtained using standard monodisperse polystyrene;

$$M_{PC} = 0.3591 M_{PS}^{1.0388}$$

wherein M_{PC} represents the molecular weight of the aromatic polycarbonate, and M_{PS} represents the molecular weight of the

polystyrene.

- Color: Using an injection molding machine, a length 50 mm × width 50 mm × thickness 3.2 mm test piece was continuously molded from the aromatic polycarbonate at a cylinder temperature of 290 °C and a mold temperature of 90 °C. The color tone of the test piece obtained was measured in accordance with the CIELAB method (Commission Internationale de l'Eclairage 1976 L*a*b* Diagram), the yellowness being given by the b* value.
- Tensile elongation: Using an injection molding machine, the aromatic polycarbonate was injection-molded at a cylinder temperature of 290 °C and a mold temperature of 90 °C. The tensile elongation (%) of the 3.2 mm-thick test piece obtained was measured in accordance with ASTM D638.
- An amount of foreign linkages was measured using the method described in WO97/32916, the alkali metal / alkaline earth metal content was measured using an ICP method, and the halogen content was measured using an ion chromatography method.

Example 1:

(1) Step (I) of continuously producing diphenyl carbonate

<First continuous multi-stage distillation column 101>

A continuous multi-stage distillation column as shown in FIG. 1 having $L_1 = 3300$ cm, $D_1 = 500$ cm, $L_1 / D_1 = 6.6$, $n_1 = 80$, $D_1 / d_{11} = 17$, and $D_1 / d_{12} = 9$ was used. In this Example, sieve trays each having a cross-sectional area per hole of approximately 1.5 cm^2 and a number of holes of approximately $250 / \text{m}^2$ were used as the internals.

<Second continuous multi-stage distillation column 201>

A continuous multi-stage distillation column as shown in FIG. 2 having $L_2 = 3100$ cm, $D_2 = 500$ cm, $L_2 / D_2 = 6.2$, $n_2 = 30$, $D_2 / d_{21} = 3.85$, and $D_2 / d_{22} = 11.1$ was used. In this Example, as the internals, two sets of Mellapak (11 theoretical stages in total) were installed in the upper portion, and sieve trays each having a cross-sectional area per hole of approximately 1.3 cm^2 and a number of holes of approximately $250 / \text{m}^2$ were used in the lower portion.

<Reactive distillation>

Diphenyl carbonate was produced by carrying out reactive distillation using an apparatus in which the first continuous multi-stage distillation column 101 and the second continuous multi-stage distillation column 201 were connected together as shown in FIG. 3.

A starting material 1 containing phenol and dimethyl carbonate in a weight ratio of phenol / dimethyl carbonate = 1.9 was introduced continuously in a liquid form at a flow rate of 50 ton / hr from an upper inlet 11 of the first continuous multi-stage distillation column 101. On the other hand, a starting material 2 containing dimethyl carbonate and phenol in a weight ratio of dimethyl carbonate / phenol = 3.6 was introduced continuously in a gaseous form at a flow rate of 50 ton / hr from a lower inlet 12 of the first continuous multi-stage distillation column 101. The molar ratio for the starting materials introduced into the first continuous multi-stage distillation column 101 was dimethyl carbonate / phenol = 1.35. The starting materials substantially did not contain halogens (outside the detection limit for the ion chromatography, i.e. not more than 1 ppb). Pb(OPh)_2 as a catalyst was introduced from the

upper inlet 11 of the first continuous multi-stage distillation column 101 such that a concentration thereof in the reaction liquid would be approximately 100 ppm. Reactive distillation was carried out continuously under conditions of a temperature at the bottom of the first continuous multi-stage distillation column 101 of 225 °C, a pressure at the top of the column of 7×10^5 Pa and a reflux ratio of 0. A first column low boiling point reaction mixture containing methanol, dimethyl carbonate, phenol and so on was continuously withdrawn in a gaseous form from the top 13 of the first column, was passed through a heat exchanger 14, and was withdrawn at a flow rate of 34 ton / hr from an outlet 16. On the other hand, a first column high boiling point reaction mixture containing methyl phenyl carbonate, dimethyl carbonate, phenol, diphenyl carbonate, the catalyst and so on was continuously withdrawn in a liquid form from the bottom 17 of the first column.

A stable steady state was attained after 24 hours. The first column high boiling point reaction mixture was thus then fed continuously as is into the second continuous multi-stage distillation column 201 at a flow rate of 66 ton / hr from a starting material inlet 21 installed between the Mellapak and the sieve trays. The liquid fed into the second continuous multi-stage distillation column 201 contained 18.2 % by weight of methyl phenyl carbonate and 0.8 % by weight of diphenyl carbonate. Reactive distillation was carried out continuously in the second continuous multi-stage distillation column 201 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. It was possible to attain stable steady state operation after 24 hours. A second column

low boiling point reaction mixture containing 35 % by weight of dimethyl carbonate and 56 % by weight of phenol was continuously withdrawn from the top 23 of the second column, the flow rate at an outlet 26 being 55.6 ton / hr, and a second column high boiling point reaction mixture containing 38.4 % by weight of methyl phenyl carbonate and 55.6 % by weight of diphenyl carbonate was continuously withdrawn from the bottom 27 of the second column. The second column low boiling point reaction mixture was continuously fed into the first continuous multi-stage distillation column 101 from the inlet 11. At this time, the amounts of fresh dimethyl carbonate and phenol newly fed into the first continuous multi-stage distillation column 101 were adjusted so as to maintain the above compositions and amounts of the starting material 1 and the starting material 2, taking into consideration the composition and amount of the second column low boiling point reaction mixture. It was found that the produced amount of diphenyl carbonate per hour was 5.74 ton. The selectivity for the diphenyl carbonate based on the phenol reacted was 98%.

Prolonged continuous operation was carried out under these conditions. The produced amounts of diphenyl carbonate per hour after 500 hours, 2000 hours, 4000 hours, 5000 hours, and 6000 hours (excluding the diphenyl carbonate contained in the starting material) were 5.74 ton, 5.75 ton, 5.74 ton, 5.74 ton, and 5.75 ton respectively, and the selectivities were 98%, 98%, 98%, 98%, and 98% respectively, and hence the operation was very stable. Moreover, the aromatic carbonates produced substantially did not contain halogens (not more than 1 ppb).

(2) Step (II) of obtaining high-purity diphenyl carbonate

<High boiling point material separating column A>

A continuous multi-stage distillation column as shown in FIG. 4 having $L_A = 1700$ cm and $D_A = 340$ cm, and having Mellapak with $n_A = 30$ installed therein as internals was used as the separating column A.

<Diphenyl carbonate purifying column B>

A continuous multi-stage distillation column as shown in FIG. 4 having $L_B = 2200$ cm and $D_B = 280$ cm, and having three sets of Mellapak with $n_{B1} = 12$, $n_{B2} = 18$, and $n_{B3} = 5$ installed therein as internals was used as the purifying column B.

Using an apparatus comprising the high boiling point material separating column A and the diphenyl carbonate purifying column B as shown in FIG. 4, the high boiling point reaction mixture from the second reactive distillation column obtained in step (I) above was continuously introduced at 13.1 ton / hr into the separating column A from an inlet A1. The column bottom temperature (T_A) was made to be 206°C and the column top pressure (P_A) was made to be 3800 Pa in the separating column A, distillation was carried out continuously with a reflux ratio of 0.6, a column top component (A_T) was continuously withdrawn at 12.5 ton / hr via a conduit 16, and a column bottom component (A_B) was continuously withdrawn at 0.6 ton / hr via a conduit 11. The column top component (A_T) was continuously introduced as is into the purifying column B from the inlet B1. The column bottom temperature (T_B) was made to be 213°C and the column top pressure (P_B) was made to be 5000 Pa in the purifying column B, distillation was carried out continuously with a reflux ratio of 1.5, a column top component (B_T) was

continuously withdrawn at 5.3 ton / hr via a conduit 26, a column bottom component (B_B) was continuously withdrawn at 0.03 ton / hr via a conduit 31, and a side cut component (B_S) was continuously withdrawn at 7.17 ton/hr via a conduit 33.

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

A_T : 6.8 % by weight of material having a lower boiling point than methyl phenyl carbonate (0.1 % by weight of dimethyl carbonate, 0.1 % by weight of anisole, 6.6 % by weight of phenol), 33.8 % by weight of methyl phenyl carbonate, 59.4 % by weight of diphenyl carbonate

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

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

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

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

produced of this high-purity diphenyl carbonate was 7.17 ton / hr.

Prolonged continuous operation was carried out under these conditions. The amount of diphenyl carbonate produced and the purity were substantially unchanged after 500 hours, 2000 hours, 4000 hours, 5000 hours, and 6000 hours.

The high-purity diphenyl carbonate obtained in this way was temporarily stored in a molten state in a storage tank.

(3) Step (III) of producing high-quality polycarbonate

Aromatic polycarbonate production was carried out using a guide-contacting downflow type polymerization apparatus as shown in FIG. 6. The material of the polymerization apparatus was all stainless steel. The polymerization apparatus had a cylindrical side casing and a tapered conical bottom portion, and was such that $L = 1,000$ cm, $h = 900$ cm, $D = 500$ cm, $d = 40$ cm, $C = 155^\circ$, and $S = 250$ m². Molten polymer fed in from a feeding port 1 was distributed uniformly by a perforated plate 2 to guides 4. An inert gas feeding port 9 was provided in a lower portion of the polymerization apparatus, and a vacuum vent 6 was provided in an upper portion. There was a jacket on the outside of the polymerization apparatus, heating being carried out using a heating medium.

An aromatic polycarbonate molten prepolymer (number average molecular weight $M_n = 4,000$) produced from bisphenol A and the high-purity diphenyl carbonate produced in steps (I) and (II) (molar ratio based on bisphenol A = 1.05) and held at 260°C was continuously fed into a feeding zone 3 from the feeding port 1 by a feed pump. The molten prepolymer, which was continuously fed into a polymerization

reaction zone 5 via the perforated plate 2 in the polymerization apparatus, was subjected to polymerization while flowing down along the guides 4. The polymerization reaction zone 5 was held at 80 Pa via the vacuum vent 6. Produced aromatic polycarbonate entering the tapered bottom portion 11 of the polymerization apparatus from the lower ends of the guides 4 was continuously withdrawn at a flow rate of 5.5 ton / hr from a discharge port 7 by a discharging pump 8 such that the amount of the aromatic polycarbonate residing in the bottom portion was nearly constant.

The number average molecular weight M_n of the aromatic polycarbonate withdrawn from an outlet 12 after 50 hours from commencement of operation was 10,500, and the aromatic polycarbonate had a good color tone ($b^* = 3.2$). Moreover, the tensile elongation was 98%. The values of M_n for the aromatic polycarbonate withdrawn from the outlet 12 after 60 hours, 100 hours, 500 hours, 1,000 hours, 2,000 hours, 3,000 hours, 4,000 hours, and 5,000 hours from commencement of operation were 10,500, 10,550, 10,500, 10,550, 10,500, 10,500, 10,550, and 10,500 respectively, and hence operation was stable.

The aromatic polycarbonate produced as above had a content of alkali metal and / or alkaline earth metal compounds of 0.04 to 0.05 ppm in terms of the metallic elements therein, and a chlorine content of not more than 1 ppb (outside the detection limit). Moreover, the content of foreign linkages was 0.12 to 0.15 mol%.

(4) Step (IV) of recycling phenol

A phenol solution containing approximately 10% of diphenyl carbonate and a trace amount of bisphenol A by-produced in step (III)

and recovered in a liquid form was continuously fed into a phenol purifying column (length 1500 cm, inside diameter 270 cm, 9 stages). Distillation was carried out continuously with a temperature at the bottom of the column of 185 °C, a pressure at the top of the column of 2000 Pa, and a reflux ratio of 0.9. Phenol recovered from the top of the column was temporarily stored in a tank, and then recycled back into step (I). Diphenyl carbonate recovered from a side cut was fed into the high boiling point material separating column of step (II), and thus recovered in the form of high-purity diphenyl carbonate.

Example 2:

(1) Step (I) of continuously producing diphenyl carbonate

Reactive distillation was carried out under the following conditions using the same apparatus as in Example 1.

A starting material 1 containing phenol and dimethyl carbonate in a weight ratio of phenol / dimethyl carbonate = 1.1 was introduced continuously in a liquid form at a flow rate of 40 ton / hr from the upper inlet 11 of the first continuous multi-stage distillation column 101. On the other hand, a starting material 2 containing dimethyl carbonate and phenol in a weight ratio of dimethyl carbonate / phenol = 3.9 was introduced continuously in a gaseous form at a flow rate of 43 ton / hr from the lower inlet 12 of the first continuous multi-stage distillation column 101. The molar ratio for the starting materials introduced into the first continuous multi-stage distillation column 101 was dimethyl carbonate / phenol = 1.87. The starting materials substantially did not contain halogens (outside the detection limit for the ion chromatography,

i.e. not more than 1 ppb). Pb(OPh)_2 as a catalyst was introduced from the upper inlet 11 of the first continuous multi-stage distillation column 101 such that a concentration thereof in the reaction liquid would be approximately 250 ppm. Reactive distillation was carried out continuously under conditions of a temperature at the bottom of the first continuous multi-stage distillation column 101 of 235°C , a pressure at the top of the column of 9×10^5 Pa and a reflux ratio of 0. A first column low boiling point reaction mixture containing methanol, dimethyl carbonate, phenol and so on was continuously withdrawn in a gaseous form from the top 13 of the first column, was passed through the heat exchanger 14, and was withdrawn at a flow rate of 43 ton / hr from the outlet 16. On the other hand, a first column high boiling point reaction mixture containing methyl phenyl carbonate, dimethyl carbonate, phenol, diphenyl carbonate, the catalyst and so on was continuously withdrawn in a liquid form from the bottom 17 of the first column.

A stable steady state was attained after 24 hours. The first column high boiling point reaction mixture was thus then fed continuously as is into the second continuous multi-stage distillation column 201 at a flow rate of 40 ton / hr from the starting material inlet 21 installed between the Mellapak and the sieve trays. The liquid fed into the second continuous multi-stage distillation column 201 contained 20.7 % by weight of methyl phenyl carbonate and 1.0 % by weight of diphenyl carbonate. Reactive distillation was carried out continuously in the second continuous multi-stage distillation column 201 under conditions of a temperature at the bottom of the column of 205°C , a pressure at the top of the column of 2×10^4 Pa, and a reflux ratio of 0.5. It was possible

to attain stable steady state operation after 24 hours. A second column low boiling point reaction mixture was continuously withdrawn from the top 23 of the second column, and a second column high boiling point reaction mixture containing 36.2 % by weight of methyl phenyl carbonate and 60.8 % by weight of diphenyl carbonate was continuously withdrawn from the bottom 27 of the second column. The second column low boiling point reaction mixture was continuously fed into the first continuous multi-stage distillation column 101 from the inlet 11. At this time, the amounts of fresh dimethyl carbonate and phenol newly fed into the first continuous multi-stage distillation column 101 were adjusted so as to maintain the above compositions and amounts of the starting material 1 and the starting material 2, taking into consideration the composition and amount of the second column low boiling point reaction mixture. It was found that the produced amount of diphenyl carbonate per hour was 4.03 ton. The selectivity for the diphenyl carbonate based on the phenol reacted was 97%.

Prolonged continuous operation was carried out under these conditions. The produced amounts of diphenyl carbonate per hour after 500 hours, 1000 hours, and 2000 hours were 4.03 ton, 4.03 ton, and 4.04 ton respectively, and the selectivities based on the reacted phenol were 97%, 97%, and 97% respectively, and hence the operation was very stable. Moreover, the aromatic carbonates produced substantially did not contain halogens (not more than 1 ppb).

(2) Step (II) of obtaining high-purity diphenyl carbonate

This was carried out using the same process as in Example 1.

(3) Step (III) of producing high-quality polycarbonate

Using the same polymerization apparatus as in Example 1, an aromatic polycarbonate molten prepolymer (number average molecular weight $M_n = 3,500$) produced from bisphenol A and the high-purity diphenyl carbonate produced in steps (I) and (II) (molar ratio based on bisphenol A = 1.05) was continuously fed into the feeding zone 3 from the feeding port 1 by the feed pump. Polymerization was carried out to produce an aromatic polycarbonate using the same process as in Example 1, except that the pressure in the polymerization reaction zone 5 was held at 100 Pa. The values of M_n for the aromatic polycarbonate discharged from a discharge port 12 after 50 hours, 100 hours, 500 hours, 1,000 hours, 2,000 hours, 3,000 hours, 4,000 hours, and 5,000 hours from commencement of operation were 7,600, 7,600, 7,650, 7,600, 7,650, 7,650, 7,600, and 7,600 respectively, and hence operation was stable.

The aromatic polycarbonate produced as above had a content of alkali metal and / or alkaline earth metal compounds of 0.03 to 0.04 ppm in terms of the metallic elements therein, and a chlorine content of not more than 1 ppb (outside the detection limit). Moreover, the content of foreign linkages was 0.08 to 0.1 mol%.

(4) Step (IV) of recycling phenol

This was carried out using the same process as in Example 1.

Example 3:

Reactive distillation was carried out under the following conditions using the same apparatus as in Example 1 except that the cross-sectional area per hole of each of the sieve trays in the second continuous multi-stage distillation column 201 was made to be

approximately 1.8 cm^2 .

A starting material 1 containing phenol and dimethyl carbonate in a weight ratio of phenol / dimethyl carbonate = 1.7 was introduced continuously in a liquid form at a flow rate of 86 ton / hr from the upper inlet 11 of the first continuous multi-stage distillation column 101. On the other hand, a starting material 2 containing dimethyl carbonate and phenol in a weight ratio of dimethyl carbonate / phenol = 3.5 was introduced continuously in a gaseous form at a flow rate of 90 ton / hr from the lower inlet 12 of the first continuous multi-stage distillation column 101. The molar ratio for the starting materials introduced into the first continuous multi-stage distillation column 101 was dimethyl carbonate / phenol = 1.44. The starting materials substantially did not contain halogens (outside the detection limit for the ion chromatography, i.e. not more than 1 ppb). $\text{Pb}(\text{OPh})_2$ as a catalyst was introduced from the upper inlet 11 of the first continuous multi-stage distillation column 101 such that a concentration thereof in the reaction liquid would be approximately 150 ppm. Reactive distillation was carried out continuously under conditions of a temperature at the bottom of the first continuous multi-stage distillation column 101 of 220°C , a pressure at the top of the column of $8 \times 10^5 \text{ Pa}$ and a reflux ratio of 0. A first column low boiling point reaction mixture containing methanol, dimethyl carbonate, phenol and so on was continuously withdrawn in a gaseous form from the top 13 of the first column, was passed through the heat exchanger 14, and was withdrawn at a flow rate of 82 ton/hr from the outlet 16. On the other hand, a first column high boiling point reaction mixture containing methyl phenyl carbonate, dimethyl carbonate, phenol, diphenyl carbonate,

the catalyst and so on was continuously withdrawn in a liquid form from the bottom 17 of the first column.

A stable steady state was attained after 24 hours. The first column high boiling point reaction mixture was thus then fed continuously as is into the second continuous multi-stage distillation column 201 at a flow rate of 94 ton / hr from the starting material inlet 21 installed between the Mellapak and the sieve trays. The liquid fed into the second continuous multi-stage distillation column 201 contained 16.0 % by weight of methyl phenyl carbonate and 0.5 % by weight of diphenyl carbonate. Reactive distillation was carried out continuously in the second continuous multi-stage distillation column 201 under conditions of a temperature at the bottom of the column of 215°C, a pressure at the top of the column of 2.5×10^4 Pa, and a reflux ratio of 0.4. It was possible to attain stable steady state operation after 24 hours. A second column low boiling point reaction mixture was continuously withdrawn from the top 23 of the second column, and a second column high boiling point reaction mixture containing 35.5 % by weight of methyl phenyl carbonate and 59.5 % by weight of diphenyl carbonate was continuously withdrawn from the bottom 27 of the second column. The second column low boiling point reaction mixture was continuously fed into the first continuous multi-stage distillation column 101 from the inlet 11. At this time, the amounts of fresh dimethyl carbonate and phenol newly fed into the first continuous multi-stage distillation column 101 were adjusted so as to maintain the above compositions and amounts of the starting material 1 and the starting material 2, taking into consideration the composition and amount of the second column low boiling point reaction

mixture. It was found that the produced amount of diphenyl carbonate per hour was 7.28 ton. The selectivity for the diphenyl carbonate based on the phenol reacted was 98%.

Prolonged continuous operation was carried out under these conditions. The produced amounts of diphenyl carbonate per hour after 500 hours, 1000 hours, and 2000 hours were 7.28 ton, 7.29 ton, and 7.29 ton respectively, and the selectivities based on the reacted phenol were 98%, 98%, and 98% respectively, and hence the operation was very stable. Moreover, the aromatic carbonates produced substantially did not contain halogens (not more than 1 ppb).

(2) Step (II) of obtaining high-purity diphenyl carbonate

This was carried out using the same process as in Example 1.

(3) Step (III) of producing high-quality polycarbonate

Aromatic polycarbonate production was carried out using a polymerization apparatus in which two guide-contacting downflow type polymerization apparatuses as shown in FIG. 6 were arranged in series. The material of each of the polymerization apparatuses was all stainless steel. The first guide-contacting downflow type polymerization apparatus had a cylindrical side casing and a tapered conical bottom portion, and was such that $L = 950$ cm, $h = 850$ cm, $D = 400$ cm, $d = 20$ cm, $C = 150^\circ$, and $S = 750$ m². The second polymerization apparatus was the same as the polymerization apparatus used in Example 1.

An aromatic polycarbonate molten prepolymer (number average molecular weight $M_n = 2,500$) produced from bisphenol A and the high-purity diphenyl carbonate produced in steps (I) and (II) (molar ratio based on bisphenol A = 1.06) was continuously fed into the feeding zone

3 from the feeding port 1 of the first polymerization apparatus by the feed pump. The molten prepolymer, which was continuously fed into the polymerization reaction zone via the perforated plate 2 in the first polymerization apparatus, was subjected to polymerization while flowing down along the guides 4. The polymerization reaction zone of the first polymerization apparatus was held at a pressure of 800 Pa via the vacuum vent 6. Aromatic polycarbonate molten prepolymer of increased polymerization degree (number average molecular weight $M_n = 5,500$) entering the tapered bottom portion 11 of the polymerization apparatus from the lower ends of the guides 4 was continuously withdrawn at a constant flow rate from the discharge port 7 by the discharging pump 8 such that the amount of the aromatic polycarbonate molten prepolymer residing in the bottom portion was nearly constant. This molten prepolymer was continuously fed into the feeding zone 3 from the feeding port 1 of the second polymerization apparatus by a feed pump. The molten prepolymer, which was continuously fed into the polymerization reaction zone via the perforated plate 2 in the second polymerization apparatus, was subjected to polymerization while flowing down along the guides 4. The polymerization reaction zone of the second polymerization apparatus was held at a pressure of 50 Pa via the vacuum vent 6. Produced aromatic polycarbonate entering the tapered bottom portion 11 of the second polymerization apparatus from the lower ends of the guides 4 was continuously withdrawn at a flow rate of 6 ton / hr from the discharge port 7 by the discharging pump 8 such that the amount of the aromatic polycarbonate residing in the bottom portion was nearly constant.

The number average molecular weight M_n of the aromatic polycarbonate withdrawn from the outlet 12 of the second polymerization apparatus after 50 hours from commencement of operation was 11,500, and the aromatic polycarbonate had a good color tone ($b^* = 3.2$). Moreover, the tensile elongation was 99%. The values of M_n for the aromatic polycarbonate withdrawn from the outlet 12 after 60 hours, 100 hours, 500 hours, 1,000 hours, 2,000 hours, 3,000 hours, 4,000 hours, and 5,000 hours from commencement of operation were 11,500, 11,550, 11,500, 11,550, 11,500, 11,500, 11,550, and 11,500 respectively, and hence operation was stable.

The aromatic polycarbonate produced as above had a content of alkali metal and / or alkaline earth metal compounds of 0.03 to 0.05 ppm in terms of the metallic elements therein, and a chlorine content of not more than 1 ppb (outside the detection limit). Moreover, the content of foreign linkages was 0.11 to 0.16 mol%.

(4) Step (IV) of recycling phenol

This was carried out using the same process as in Example 1.

Industrial Applicability

It has been discovered that, when producing the aromatic polycarbonate from the dialkyl carbonate and the aromatic dihydroxy compound, by implementing the process according to the present invention which comprises the steps of: (I) producing a diphenyl carbonate using two reactive distillation columns each having a specified structure; (II) purifying the diphenyl carbonate by using a high boiling point material separating column A and a diphenyl carbonate purifying

column B each having a specified structure so as to obtain a high-purity diphenyl carbonate from the diphenyl carbonate; (III) subsequent producing an aromatic polycarbonate by using a guide-contacting downflow type polymerization apparatus having a specified structure from a molten prepolymer obtained from an aromatic dihydroxy compound and the high-purity diphenyl carbonate; and (IV) recycling by-produced phenol into the step (I), a high-quality high-performance aromatic polycarbonate having excellent mechanical properties and no coloration can be produced on an industrial scale of not less than 1 ton / hr at a fast polymerization rate. Moreover, it has been discovered that a high-quality aromatic polycarbonate can be produced stably for a prolonged period of time of, for example not less than 2000 hours, preferably not less than 3000 hours, more preferably not less than 5000 hours, with little variation in molecular weight. The present invention thus provides a process that achieves excellent effects as an industrial process for the production of a high-quality aromatic polycarbonate.

CLAIMS

We claim:

1. An industrial process for the production of a high-quality aromatic polycarbonate in which an aromatic polycarbonate is continuously produced from a dialkyl carbonate and an aromatic dihydroxy compound, the process comprising the steps of:

(I) continuously producing a diphenyl carbonate by taking the dialkyl carbonate and a phenol as a starting material, continuously feeding the starting material into a first continuous multi-stage distillation column in which a homogeneous catalyst is present, carrying out reaction and distillation simultaneously in said first column, continuously withdrawing a first column low boiling point reaction mixture containing a produced alcohol from an upper portion of said first column in a gaseous form, continuously withdrawing a first column high boiling point reaction mixture containing a produced alkyl phenyl carbonate from a lower portion of said first column in a liquid form, continuously feeding said first column high boiling point reaction mixture into a second continuous multi-stage distillation column in which a catalyst is present, carrying out reaction and distillation simultaneously in said second column, continuously withdrawing a second column low boiling point reaction mixture containing a produced dialkyl carbonate from an upper portion of said second column in a gaseous form, continuously withdrawing a second column high boiling point reaction mixture containing a produced diphenyl carbonate from a lower portion of said second column in a liquid form, and continuously feeding the second column low boiling point

reaction mixture containing the dialkyl carbonate into the first continuous multi-stage distillation column;

(II) purifying the diphenyl carbonate by continuously introducing the second column high boiling point reaction mixture containing the diphenyl carbonate into a high boiling point material separating column A, and continuously carrying out separation by distillation into a column top component A_T containing the diphenyl carbonate and a column bottom component A_B containing the catalyst, and then continuously introducing said column top component A_T into a diphenyl carbonate purifying column B having a side cut outlet, and continuously carrying out separation by distillation into three components being a column top component B_T , a side cut component B_S and a column bottom component B_B , so as to obtain a high-purity diphenyl carbonate as the side cut component;

(III) producing the aromatic polycarbonate by reacting said aromatic dihydroxy compound and said high-purity diphenyl carbonate together so as to produce an aromatic polycarbonate molten prepolymer, and said molten prepolymer being made to flow down along surfaces of guides by using a guide-contacting downflow type polymerization apparatus, so as to polymerize said molten prepolymer while flowing down; and

(IV) recycling a phenol by circulating phenol by-produced in step (III) back into the diphenyl carbonate production step (I);

wherein:

(a) said first continuous multi-stage distillation column comprises a structure having a cylindrical trunk portion having a length L_1 (cm) and an inside diameter D_1 (cm), and having an internal with number of stages

n_1 thereinside, and comprises a gas outlet having an inside diameter d_{11} (cm) at a top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_{12} (cm) at a bottom of the column or in a lower portion of the column near to the bottom, at least one first inlet provided in the upper portion and / or a middle portion of the column below said gas outlet, and at least one second inlet provided in the middle portion and / or the lower portion of the column above said liquid outlet, wherein L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} respectively satisfy the following formulae (1) to (6);

$$1500 \leq L_1 \leq 8000 \quad (1),$$

$$100 \leq D_1 \leq 2000 \quad (2),$$

$$2 \leq L_1 / D_1 \leq 40 \quad (3),$$

$$20 \leq n_1 \leq 120 \quad (4),$$

$$5 \leq D_1 / d_{11} \leq 30 \quad (5), \text{ and}$$

$$3 \leq D_1 / d_{12} \leq 20 \quad (6);$$

(b) said second continuous multi-stage distillation column comprises a structure having a cylindrical trunk portion having a length L_2 (cm) and an inside diameter D_2 (cm), and having an internal with number of stages n_2 thereinside, and comprises a gas outlet having an inside diameter d_{21} (cm) at a top of the column or in an upper portion of the column near to the top, a liquid outlet having an inside diameter d_{22} (cm) at a bottom of the column or in a lower portion of the column near to the bottom, at least one third inlet provided in the upper portion and / or a middle portion of the column below said gas outlet, and at least one fourth inlet provided in the middle portion and / or the lower portion of the column above said liquid outlet, wherein L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} ,

and D_2 / d_{22} respectively satisfy the following formulae (7) to (12);

$$1500 \leq L_2 \leq 8000 \quad (7),$$

$$100 \leq D_2 \leq 2000 \quad (8),$$

$$2 \leq L_2 / D_2 \leq 40 \quad (9),$$

$$10 \leq n_2 \leq 80 \quad (10),$$

$$2 \leq D_2 / d_{21} \leq 15 \quad (11), \text{ and}$$

$$5 \leq D_2 / d_{22} \leq 30 \quad (12);$$

(c) said high boiling point material separating column A is a continuous multi-stage distillation column having a length L_A (cm) and an inside diameter D_A (cm), and having an internal with number of stages n_A thereinside, wherein L_A , D_A , and n_A satisfy the following formulae (13) to (15);

$$800 \leq L_A \leq 3000 \quad (13),$$

$$100 \leq D_A \leq 1000 \quad (14), \text{ and}$$

$$20 \leq n_A \leq 100 \quad (15),$$

and said diphenyl carbonate purifying column B is a continuous multi-stage distillation column having a length L_B (cm) and an inside diameter D_B (cm), having an internal thereinside, having an inlet B1 at a middle stage of the column, and a side cut outlet B2 between said inlet B1 and the column bottom, and having number of stages n_{B1} of the internal above the inlet B1, number of stages n_{B2} of the internal between the inlet B1 and the side cut outlet B2, number of stages n_{B3} of the internal below the side cut outlet B2, and a total number of stages n_B ($= n_{B1} + n_{B2} + n_{B3}$), wherein L_B , D_B , n_{B1} , n_{B2} , n_{B3} , and n_B satisfy the following formulae (16) to (21);

$$1000 \leq L_B \leq 5000 \quad (16),$$

$$100 \leq D_B \leq 1000 \quad (17),$$

$$5 \leq n_{B1} \leq 20 \quad (18),$$

$$12 \leq n_{B2} \leq 40 \quad (19),$$

$$3 \leq n_{B3} \leq 15 \quad (20), \text{ and}$$

$$20 \leq n_B \leq 70 \quad (21);$$

(d) said guide-contacting downflow type polymerization apparatus comprises:

(1) an apparatus having a molten prepolymer receiving port, a perforated plate, a polymerization reaction zone having a plurality of guides that extend downward from the perforated plate provided in a space surrounded by the perforated plate, a side casing and a tapered bottom casing, a molten prepolymer feeding zone for feeding the molten prepolymer via the perforated plate onto the guides in the polymerization reaction zone, a vacuum vent provided in the polymerization reaction zone, an aromatic polycarbonate discharge port provided in a lowermost portion of the tapered bottom casing, and an aromatic polycarbonate discharge pump connected to the discharge port, wherein:

(2) an internal sectional area A (m^2) taken through a horizontal plane of the side casing in the polymerization reaction zone satisfies the formula (22),

$$0.7 \leq A \leq 300 \quad (22),$$

(3) a ratio between A (m^2) and an internal sectional area B (m^2) taken through a horizontal plane of the aromatic polycarbonate discharge port satisfies the formula (23),

$$20 \leq A / B \leq 1000 \quad (23),$$

(4) the tapered bottom casing in the polymerization reaction zone

is connected at an internal angle C ($^{\circ}$) to the side casing thereabove, wherein the angle C ($^{\circ}$) satisfies the formula (24),

$$120 \leq C \leq 165 \quad (24),$$

(5) a length h (cm) of each guide satisfies the formula (25),

$$150 \leq h \leq 5000 \quad (25), \text{ and}$$

(6) a total external surface area S (m^2) of said guide satisfies the formula (26),

$$2 \leq S \leq 50000 \quad (26).$$

2. The process according to Claim 1, wherein not less than 1 ton / hr of the aromatic polycarbonate is produced.

3. The process according to Claim 1 or 2, wherein said d_{11} and said d_{12} satisfy the formula (27), and said d_{21} and said d_{22} satisfy the formula (28);

$$1 \leq d_{12} / d_{11} \leq 5 \quad (27); \text{ and}$$

$$1 \leq d_{21} / d_{22} \leq 6 \quad (28).$$

4. The process according to any one of Claims 1 to 3, wherein L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} for said first continuous multi-stage distillation column satisfy respectively $2000 \leq L_1 \leq 6000$, $150 \leq D_1 \leq 1000$, $3 \leq L_1 / D_1 \leq 30$, $30 \leq n_1 \leq 100$, $8 \leq D_1 / d_{11} \leq 25$, and $5 \leq D_1 / d_{12} \leq 18$, and L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} , and D_2 / d_{22} for said second continuous multi-stage distillation column satisfy respectively $2000 \leq L_2 \leq 6000$, $150 \leq D_2 \leq 1000$, $3 \leq L_2 / D_2 \leq 30$, $15 \leq n_2 \leq 60$, $2.5 \leq D_2 / d_{21} \leq 12$, and $7 \leq D_2 / d_{22} \leq 25$.

5. The process according to any one of Claims 1 to 4, wherein L_1 , D_1 , L_1 / D_1 , n_1 , D_1 / d_{11} , and D_1 / d_{12} for said first continuous multi-stage distillation column satisfy respectively $2500 \leq L_1 \leq 5000$, $200 \leq D_1 \leq 800$, $5 \leq L_1 / D_1 \leq 15$, $40 \leq n_1 \leq 90$, $10 \leq D_1 / d_{11} \leq 25$, and $7 \leq D_1 / d_{12} \leq 15$, and L_2 , D_2 , L_2 / D_2 , n_2 , D_2 / d_{21} , and D_2 / d_{22} for said second continuous multi-stage distillation column satisfy respectively $2500 \leq L_2 \leq 5000$, $200 \leq D_2 \leq 800$, $5 \leq L_2 / D_2 \leq 15$, $20 \leq n_2 \leq 50$, $3 \leq D_2 / d_{21} \leq 10$, and $9 \leq D_2 / d_{22} \leq 20$.

6. The process according to any one of Claims 1 to 5, wherein each of said first continuous multi-stage distillation column and said second continuous multi-stage distillation column is a distillation column having a tray and / or a packing as said internal.

7. The process according to Claim 6, wherein said first continuous multi-stage distillation column is a plate type distillation column having the tray as said internal, and said second continuous multi-stage distillation column is a distillation column having both the packing and the tray as said internal.

8. The process according to Claim 6 or 7, wherein each tray in said first continuous multi-stage distillation column and said second continuous multi-stage distillation column is a sieve tray having a sieve portion and a downcomer portion.

9. The process according to Claim 8, wherein each sieve tray has 100 to 1000 holes / m² in said sieve portion.

10. The process according to Claim 8 or 9, wherein a cross-sectional area per hole of each sieve tray is in a range of from 0.5 to 5 cm².

11. The process according to Claim 6 or 7, wherein said second continuous multi-stage distillation column is a distillation column having, as said internal, the packing in the upper portion of the column, and the tray in the lower portion of the column.

12. The process according to any one of Claims 6 to 11, wherein said packing of said internal in said second continuous multi-stage distillation column is one or a plurality of sets of structured packings.

13. The process according to Claim 12, wherein the structured packing in said second continuous multi-stage distillation column is at least one type selected from the group consisting of Mellapak, Gempak, Techno-pack, Flexipac, a Sulzer packing, a Goodroll packing, and Glitschgrid.

14. The process according to any one of Claims 1 to 13, wherein each of said high boiling point material separating column A and said diphenyl carbonate purifying column B is a distillation column having

a tray and/or a packing as said internal.

15. The process according to Claim 14, wherein the internal of each of said high boiling point material separating column A and said diphenyl carbonate purifying column B is the packing.

16. The process according to Claim 15, wherein the packing is a structured packing of at least one type selected the group consisting of Mellapak, Gempak, Techno-pack, Flexipac, a Sulzer packing, a Goodroll packing, and Glitschgrid.

17. The process according to any one of Claims 1 to 16, wherein, the side casing in the polymerization reaction zone is cylindrical with an inside diameter D (cm) and a length L (cm), the tapered bottom casing, which is connected to the lower portion of the side casing, is conical, and the discharge port, which is in the lowermost portion of said tapered conical bottom casing, is cylindrical with an inside diameter d (cm), wherein D , L and d satisfy the following formulae (29), (30), (31) and (32);

$$100 \leq D \leq 1800 \quad (29),$$

$$5 \leq D / d \leq 50 \quad (30),$$

$$0.5 \leq L / D \leq 30 \quad (31), \text{ and}$$

$$h - 20 \leq L \leq h + 300 \quad (32).$$

18. The process according to any one of Claims 1 to 17, wherein said h satisfies the formula (33);

$$400 < h \leq 2500 \quad (33).$$

19. The process according to any one of Claims 1 to 18, wherein each guide is cylindrical, or pipe-shaped and made to be such that the molten prepolymer cannot enter therein, with an outside diameter r (cm), wherein r satisfies the formula (34);

$$0.1 \leq r \leq 1 \quad (34).$$

20. The process according to any one of Claims 1 to 19, wherein the polymerization is carried out using two or more of said guide-contacting downflow type polymerization apparatuses linked together.

21. The process according to any of Claims 1 to 20, wherein the plurality of the guide-contacting downflow type polymerization apparatuses according to claim 17 comprise two polymerization apparatuses being a first guide-contacting downflow type polymerization apparatus and a second guide-contacting downflow type polymerization apparatus, wherein in a process in which a polymerization degree is increased in this order, a total external surface area $S1$ (m^2) of the guides in said first guide-contacting downflow type polymerization apparatus and a total external surface area $S2$ (m^2) of the guides in said second guide-contacting downflow type polymerization apparatus satisfy the formula (35);

$$1 \leq S1 / S2 \leq 20 \quad (35).$$

22. A high-quality aromatic polycarbonate produced in an amount of not less than 1 ton / hr, which is produced by the process according to any of Claims 1 to 21.

23. The high-quality aromatic polycarbonate according to Claim 22, having a content of alkali metal and / or alkaline earth metal compounds in a range of from 0.1 to 0.01 ppm in terms of metallic elements therein, and a halogen content of not more than 1 ppb.

24. The high-quality aromatic polycarbonate according to Claim 22 or 23, being an aromatic polycarbonate having a main chain thereof partially branched through a foreign linkage including an ester linkage or an ether linkage, and having a content of said foreign linkage in a range of from 0.05 to 0.5 mol% based on carbonate linkages.