SPECIFICATION

PROCESS FOR PRODUCING AROMATIC POLYCARBONATE RESIN

TECHNICAL FIELD

[0001]

The present invention relates to a process for producing an aromatic polycarbonate resin. More particularly, the present invention relates to a process for producing an aromatic polycarbonate resin having a less content of foreign matters by using a specific polymer filter, and further to a process for producing aromatic polycarbonate resins which is capable of providing products of different grades that are different in viscosity-average molecular weight (Mv) or branching degree from each other by switching an operation of the process by changing reaction conditions in a transesterification method.

BACKGROUND ART

[0002]

Aromatic polycarbonate resins have been extensively used in various applications because they are excellent in heat resistance, mechanical properties such as impact resistance, dimensional stability and transparency.

[0003]

As the method for producing the aromatic polycarbonate

resins, there are known a melt polymerization method (transesterification method), an interfacial polymerization method (phosgene method), etc. However, in any of these conventional methods, since foreign matters are generated in a reaction apparatus or a flow path of high-viscous substances after the reaction, it is required to remove the foreign matters therefrom. For this reason, there has been adopted the method of treating a molten aromatic polycarbonate resin with a polymer filter, and various proposals for such a method have been reported.

[0004]

For example, there have been proposed the method of purging a filter housing and metal elements with water or nitrogen (Patent Documents 1 and 2); the treating method conducted under a specific differential pressure using a filter retaining particles having a specific particle diameter (Patent Document 3); the method using a filter having a specific structure (Patent Document 4); and the method using one or more filter devices accommodating a laminate constituted from a plurality of disc-type filter elements in which each filter element has an outer diameter of not more than 15 inches (38.1 cm), a ratio of an inner diameter to the outer diameter (inner diameter/outer diameter) of not less than 1/7, and a mesh size of not more than 40 μm (Patent Document 5). These proposed methods are

based on the finding that when air retained in the filter is contacted with a molten resin, the resin undergoes thermal decomposition to thereby generate gelled substances (Patent Documents 1 and 2), or the finding that the resin is retained and deteriorated in the filter (Patent Documents 3 to 5).

[0005]

In addition, as to the method of mixing and melting an aromatic dihydroxy compound and a carbonic diester and then filtering the resulting melted mixture which is to be conducted prior to the melt polycondensation, there has been proposed the method in which a filter used therein is treated by any one of a method of washing the filter with a washing solution comprising at least one acid selected from the group consisting of orthophosphoric acid, nitric acid and oxalic acid, and a method of aging the filter at a temperature of 150 to 250°C for 12 to 48 hr (Patent Document 6). This method has been proposed to avoid such a disadvantage that when treating an aromatic polycarbonate resin with a polymer filter, the polymer filter is heated to a temperature far higher than a melting point of the polymer owing to a pressure loss, thereby causing formation of gels or decomposition or carbonization of the polycarbonate.

[0006]

In the transesterification method, the aromatic

polycarbonate resin is produced by subjecting the aromatic dihydroxy compound and the carbonic diester both kept in a molten state to polycondensation in the presence of a catalyst while removing phenols by-produced, from the reaction system. In the case where it is intended to obtain products of different grades that are different in viscosity-average molecular weight (Mv) or branching degree from each other, operation is switched by changing reaction (polycondensation) conditions in a series of processes using a single production facility. For example, when the mode of operation is switched from production of the product having a large Mv to production of the product having a small Mv, from the viewpoint of a good productivity, it is important to shorten a time required until returning to a steady state (such a state in which the on-specification product having a small Mv is obtained after adverse influence of the previous reaction conditions is dissipated).

[0007]

As the method of producing the aromatic polycarbonate resins in which the operation is switched in such a manner as described above, there has been proposed the improved method of tracing or monitoring the number of fisheyes in the aromatic polycarbonate resin and determining the time for conducting a procedure for cleaning a gas phase of a reactor (Patent Document 7).

[0008]

According to the above method, since the time for conducting a procedure for cleaning a gas phase of a reactor can be adequately determined, it is possible to produce the aromatic polycarbonate resin having a less number of fisheyes and exhibiting an excellent hue in an efficient manner. However, the method fails to take into account how to shorten the time required until returning to a steady state after switching the operation.

[0009]

Patent Document 1: Japanese Patent Application Laid-open (KOKAI) No. 11-291237(1999)

Patent Document 2: Japanese Patent Application Laid-open (KOKAI) No. 11-291304(1999)

Patent Document 3: Japanese Patent Application Laid-open (KOKAI) No. 2000-219737

Patent Document 4: Japanese Patent Application Laid-open (KOKAI) No. 2001-9214

Patent Document 5: PCT Pamphlet WO 01/83584

Patent Document 6: Japanese Patent Application Laid-open (KOKAI) No. 2003-48975

Patent Document 7: Japanese Patent Application Laid-open (KOKAI) No. 2007-31621

DISCLOSURE OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0010]

An object of the present invention is to provide a process for producing an aromatic polycarbonate resin (purified aromatic polycarbonate resin) having a less content of foreign matters or phenols which is prevented from suffering from prolonged retention and deterioration of the resin in a filter.

[0011]

Another object of the present invention is to provide an improved process for producing aromatic polycarbonate resins in which products of different grades that are different in viscosity-average molecular weight (Mv) or branching degree from each other are obtained by switching operation of the process by changing reaction conditions in transesterification method, wherein the time required until returning to a steady state after switching the operation can be shortened to thereby produce the aromatic polycarbonate resin having a less number of fisheyes and exhibiting an excellent hue in an efficient manner.

MEANS FOR SOLVING THE PROBLEM

[0012]

As a result of the present inventors' earnest study, it has been found that when modifying a filter such that an

outermost surface thereof is kept in a specific condition, the resin to be treated therewith can be prevented from suffering from prolonged retention and deterioration in the filter as well as undesirable catalytic action due to constitutional metals of the filter, thereby obtaining an aromatic polycarbonate resin having a less content of foreign matters or phenols.

[0013]

The present invention has been attained on the basis of the above finding. That is, in an aspect of the present invention, there is provided a process for producing a purified aromatic polycarbonate resin, comprising the step of treating a molten aromatic polycarbonate resin with a polymer filter, wherein a concentration ratio of a chromium atom to an iron atom (Cr/Fe) which are present on an outermost surface of the polymer filter as measured by X-ray photoelectron spectroscopy is not less than 1.5 (first invention).

[0014]

In another aspect of the present invention, there is provided a process for producing aromatic polycarbonate resins in which after producing a polycarbonate resin A having a viscosity-average molecular weight Ma, production conditions are changed to produce a polycarbonate resin B having a viscosity-average molecular weight Mb smaller than

the viscosity-average molecular weight Ma using the same production facilities as used for production of the polycarbonate resin A, said process comprising at least a polycondensation step of conducting transesterification reaction of an aromatic dihydroxy compound with a carbonic diester compound and a purification step of allowing the resulting molten aromatic polycarbonate resin to pass through a polymer filter using a melting extruder to remove foreign matters therefrom, wherein a filter having a larger mesh size (opening diameter) is used as the polymer filter when producing the polycarbonate resin A, and a filter having a smaller mesh size (opening diameter) is used as the polymer filter when producing the polycarbonate resin B; when switching operation of the process from production of the polycarbonate resin A to production of the polycarbonate resin B, the polymer filter having a larger mesh size is changed-over to the polymer filter having a smaller mesh size; and a difference between the number of fisheyes in the resin as measured 2 hr before changing over the polymer filters and that as measured 1 hr before changing over the polymer filters, is not more than 10 (second invention).

[0015]

Further, in the other aspect of the present invention, there is provided a process for producing aromatic polycarbonate resins in which after producing a

polycarbonate resin C having a branching degree Nc, production conditions are changed to produce a polycarbonate resin D having a branching degree Nd smaller than the branching degree Nc using the same production facilities as used for production of the polycarbonate resin C, said process comprising at least a polycondensation step of conducting transesterification reaction of an aromatic dihydroxy compound with a carbonic diester compound and a purification step of allowing the resulting molten aromatic polycarbonate resin to pass through a polymer filter using a melting extruder to remove foreign matters therefrom, wherein a filter having a larger mesh size (opening diameter) is used as the polymer filter when producing the polycarbonate resin C, and a filter having a smaller mesh size (opening diameter) is used as the polymer filter when producing the polycarbonate resin D; when switching operation of the process from production of the polycarbonate resin C to production of the polycarbonate resin D, the polymer filter having a larger mesh size is changed over to the filter having a smaller mesh size; and a difference between the number of fisheyes in the resin as measured 2 hr before changing over the polymer filters and that as measured 1 hr before changing over the polymer filters, is not more than 10 (third invention).

EFFECT OF THE INVENTION

[0016]

According to the first invention, it is possible to produce an aromatic polycarbonate resin having a less content of foreign matter or phenols. According to the second and third inventions, it is possible to produce aromatic polycarbonate resins having a less number of fisheyes and exhibiting an excellent hue in an efficient manner, which are obtained as products of different grades that are different in viscosity-average molecular weight or branching degree from each other.

PREFERRED EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0017]

The present invention is described in detail below. The aromatic polycarbonate resin used in the present invention includes branched or unbranched thermoplastic polycarbonate polymers or copolymers which are produced by reacting an aromatic hydroxy compound or a mixture of the aromatic hydroxy compound and a small amount of a polyhydroxy compound with phosgene or a carbonic diester.

[0018]

The aromatic polycarbonate resin may be produced by conventionally known methods such as, for example, a melt polymerization method (transesterification method) and an

interfacial polymerization method (phosgene method). Further, according to the melt polymerization method, there may be produced such an aromatic polycarbonate resin in which the amount of end hydroxyl groups is well controlled.

[0019]

Examples of the aromatic dihydroxy compound used as the raw material of the aromatic polycarbonate resin may include bis(hydroxyaryl)alkanes such as 2,2-bis(4-hydroxyphenyl)propane (alias: bisphenol A), 2,2-bis(3,5-bibromo-4-hydroxyphenyl)propane (alias: tetrabromobisphenol A), bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)octane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 1,1-bis(3-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 2,2-bis(3-bromo-4-hydroxyphenyl)propane, 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane, 2,2-bis(3-phenyl-4-hydroxyphenyl)propane, 2,2-bis(3-cyclohexyl-4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, bis(4-hydroxyphenyl)diphenylmethane, 2,2-bis(4-hydroxyphenyl)-1,1,1-trichloropropane, 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexachloropropane and 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane; bis(hydroxyaryl)cycloalkanes such as 1,1-bis(4-

hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane; bisphenols having a cardo structure such as 9,9-bis(4-hydroxyphenyl)fluorene and 9,9-bis(4-hydroxy-3-methylphenyl)fluorene; dihydroxydiaryl ethers such as 4,4'-dihydroxydiphenyl ether and 4,4'-dihydroxy-3,3'-dimethyldiphenyl ether; dihydroxydiaryl sulfides such as 4,4'-dihydroxydiphenyl sulfide and 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfide; dihydroxydiaryl sulfoxides such as 4,4'-dihydroxydiphenyl sulfoxide and 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfoxide; dihydroxydiaryl sulfones such as 4,4'-dihydroxydiphenyl sulfone and 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfone; hydroquinone; resorcin; and 4,4'-dihydroxydiphenyl. Among these aromatic dihydroxy compounds, preferred are bis(4-hydroxyphenyl)alkanes, and more preferred is bisphenol A from the viewpoint of a good impact resistance of the resultant aromatic polycarbonate resin. In addition, for the purpose of enhancing a flame retardancy of the resultant aromatic polycarbonate resin, there may also be used those compounds formed by bonding one or more sulfonic acid tetraalkyl phosphonium groups to the above aromatic dihydroxy compounds. These aromatic dihydroxy compounds may be used in combination of any two or more thereof.

[0020]

The branched aromatic polycarbonate resin may be obtained by such an interfacial polymerization method in which a part of the above aromatic dihydroxy compound is replaced with a polyhydroxy compound such as fluoroglucin, 4,6-dimethyl-2,4,6-tris(4-hydroxyphenyl)heptene-2, 4,6-dimethyl-2,4,6-tris(4-hydroxyphenyl)heptane, 2,6-dimethyl-2,4,6-tris(4-hydroxyphenyl)heptene-3, 1,3,5-tris(4-hydroxyphenyl)benzene and 1,1,1-tris(4-hydroxyphenyl)ethane, or 3,3-bis(4-hydroxyaryl)oxyindole (alias: isatin bisphenol), 5-chloroisatin, 5,7-dichloroisatin, 5-bromoisatin, etc. The amount of the polyhydroxy compound or the like with which a part of the aromatic dihydroxy compound is replaced is usually 0.01 to 10 mol% and preferably 0.1 to 2 mol% on the basis of the aromatic dihydroxy compound. On the other hand, in the melt polymerization method, the branched aromatic polycarbonate resin may be obtained by optionally adding the above branching agent and well controlling the reaction temperature and the amount of the catalyst used.

[0021]

The reaction by the interfacial polymerization method may be conducted in the following manner by using the aromatic dihydroxy compound, optionally together with a molecular weight controller (end stopping agent) and an antioxidant for preventing oxidation of the aromatic dihydroxy compound. That is, the aromatic dihydroxy

compound is reacted with phosgene in the presence of an organic solvent inert to the reaction and an alkali aqueous solution while maintaining the reaction system at a pH of usually not less than 9, and then a polymerization catalyst such as a tertiary amine and a quaternary ammonium salt is added to the reaction system to conduct the interfacial polymerization, thereby obtaining a polycarbonate. Meanwhile, the reaction temperature is, for example, 0 to 40°C, and the reaction time is, for example, from several minutes (for example, 10 min) to several hours (for example, 6 hr).

[0022]

Examples of the organic solvent inert to the reaction may include chlorinated hydrocarbons such as methylene chloride, 1,2-dichloroethane, chloroform, monochlorobenzene and dichlorobenzene; and aromatic hydrocarbons such as benzene, toluene and xylene. Examples of the alkali compound used in the alkali aqueous solution may include hydroxides of alkali metals such as sodium hydroxide and potassium hydroxide.

[0023]

Examples of the molecular weight controller may include compounds having a monovalent phenolic hydroxyl group. Specific examples of the molecular weight controller may include m-methyl phenol, p-methyl phenol, m-propyl phenol,

p-propyl phenol, p-tert-butyl phenol and p-long chain alkyl-substituted phenols. The amount of the molecular weight controller used is usually 50 to 0.5 mol and preferably 30 to 1 mol on the basis of 100 mol of the aromatic dihydroxy compound.

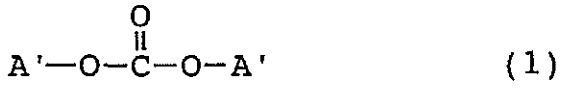
[0024]

The melting transesterification method may be conducted, for example, by subjecting the carbonic diester and the aromatic dihydroxy compound to transesterification reaction.

[0025]

Examples of the carbonic diester may include compounds represented by the following general formula (1):

[0026]



(1)

[0027]

In the general formula (1), A' is a substituted or unsubstituted, linear, branched or cyclic monovalent hydrocarbon group having 1 to 10 carbon atoms. The two A' groups may be the same or different. Meanwhile, examples of the substituent group which may be bonded to the A' group may include 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 and a nitro group.

[0028]

Specific examples of the carbonic diester may include diphenyl carbonate, substituted diphenyl carbonates such as ditolyl carbonate, and dialkyl carbonates such as dimethyl carbonate, diethyl carbonate and di-tert-butyl carbonate. Among these carbonic diesters, preferred are diphenyl carbonate (hereinafter referred to merely as "DPC") and substituted diphenyl carbonates. These carbonic diesters may be used in the form of a mixture of any two or more thereof.

[0029]

In addition, a part of the above carbonic diester may be replaced with a dicarboxylic acid or a dicarboxylic acid ester. The proportion of the dicarboxylic acid or the dicarboxylic acid ester with which a part of the carbonic diester may be replaced, is usually not more than 50 mol% and preferably not more than 30 mol%. Typical examples of the dicarboxylic acid or the dicarboxylic acid ester may include terephthalic acid, isophthalic acid, diphenyl terephthalate and diphenyl isophthalate. When a part of the carbonic diester is replaced with these compounds, the obtained transesterification reaction products are polyester carbonates.

[0030]

Also, upon producing the polycarbonates by a transesterification method, the carbonic diester (including

the dicarboxylic acid or the dicarboxylic acid ester used for replacing a part of the carbonic diester; this is similarly applied to the subsequent descriptions) is used in an excessive amount relative to the aromatic dihydroxy compound. That is, the ratio (molar ratio) of the carbonic diester to the aromatic dihydroxy compound is usually 1.00 to 1.30, preferably 1.01 to 1.20 and more preferably 1.05 to 1.20. When the molar ratio is too small, the content of end hydroxyl groups in the resultant aromatic polycarbonates tends to be increased, resulting in deteriorated thermal stability of the resins. Whereas, when the molar ratio is too large, the transesterification reaction rate tends to be lowered, so that it tends to be difficult to produce aromatic polycarbonates having a desired molecular weight. Further, since the amount of the residual carbonic diester in the obtained resins is increased, off-odor tends to be generated upon molding or from the resultant molded product. Therefore, the content of the end hydroxyl groups in the obtained aromatic polycarbonates is preferably not less than 100 ppm. By controlling the content of the end hydroxyl groups to the above specified range, it is possible to prevent reduction in molecular weight of the obtained aromatic polycarbonates and allowing the aromatic polycarbonates to exhibit a more excellent color tone.

[0031]

In general, the polycarbonates having a desired molecular weight and a desired content of the end hydroxy groups may be obtained by suitably controlling a mixing ratio between the carbonic diester and the aromatic dihydroxy compound or adjusting a degree of vacuum used upon the reaction. As the more positive method, there may be used such a known control method in which an end stopping agent is separately added upon the reaction. Examples of the end stopping agent used in the above method may include monovalent phenols, monovalent carboxylic acids and carbonic diesters. The content of the end hydroxyl groups in the polycarbonates has a large influence on thermal stability, hydrolysis stability, color tone, etc., of the polycarbonate products. The content of the end hydroxyl groups in the polycarbonates varies depending upon applications thereof, and is usually not more than 1,000 ppm and preferably not more than 700 ppm in order to allow the polycarbonates to exhibit practical properties.

[0032]

When producing the polycarbonates by a transesterification method, the transesterification is usually conducted in the presence of a transesterification catalyst. The transesterification catalyst used in the above method is not particularly limited, and is preferably an alkali metal compound and/or an alkali earth metal

compound. The transesterification catalyst may be used in combination with a basic compound as an auxiliary component such as a basic boron compound, a basic phosphorus compound, a basic ammonium compound and an amine-based compound. Among these transesterification catalysts, from the practical viewpoint, preferred are alkali metal compounds. These transesterification catalysts may be used in combination of any two or more thereof. The amount of the transesterification catalyst used is in the range of usually 1×10^{-9} to 1×10^{-1} mol, preferably 1×10^{-7} to 1×10^{-3} mol and more preferably 1×10^{-7} to 1×10^{-6} mol on the basis of 1 mol of the aromatic dihydroxy compound.

[0033]

Examples of the alkali metal compounds may include inorganic alkali metal compounds such as hydroxides, carbonates and hydrogencarbonate compounds of alkali metals; and organic alkali metal compounds such as salts of alkali metals with alcohols (or phenols) or organic carboxylic acids. Examples of the alkali metal used in the alkali metal compounds may include lithium, sodium, potassium, rubidium and cesium. Among these alkali metal compounds, preferred are cesium compounds, and more preferred are cesium carbonate, cesium hydrogencarbonate and cesium hydroxide.

[0034]

The transesterification reaction between the aromatic dihydroxy compound and the carbonic diester may be conducted in the following manner.

[0035]

First, in the raw material preparation step, a mixed melt solution of the raw materials is prepared in an inert gas atmosphere such as nitrogen and argon using a batch-type, semi-batch-type or continuous-type stirring vessel apparatus. For example, when using bisphenol A as the aromatic dihydroxy compound and diphenyl carbonate as the carbonic diester, the temperature used upon the melting and mixing is in the range of usually 120 to 180°C and preferably 125 to 160°C.

[0036]

Next, in the polycondensation step, the aromatic dihydroxy compound and the carbonic diester compound are subjected to transesterification reaction. The transesterification reaction is continuously conducted in a multi-stage manner, usually in two or more stages and preferably in 3 to 7 stages. Specific reaction conditions in the respective stage vessels include temperature: 150 to 320°C; pressure: from normal pressures to reduced pressure (1.01×10^6 Pa to 1.3 Pa); and average residence time: 5 to 150 min.

[0037]

In the respective reactors used in the multi-stage operation, in order to effectively remove phenols by-produced with the proceeding of the polycondensation reaction out of the reaction system, the temperature and the degree of vacuum is stepwise increased within the ranges of the above specified reaction conditions, and finally the pressure is reduced to not more than 2 Torr (266.6 Pa), whereby the melt polycondensation reaction can be conducted while removing the by-products such as aromatic hydroxy compounds from the reaction system. Meanwhile, in order to prevent the obtained aromatic polycarbonates from being deteriorated in quality such as hue, the reaction temperature and the residence time are preferably kept as low as possible and as short as possible, respectively, within the ranges of the above specified reaction conditions. [0038]

The melt-polycondensation may be conducted by either a batch method or a continuous method, and is preferably conducted by a continuous method from the viewpoint of a good stability of the resin composition of the present invention. Examples of a deactivator for the catalyst may include compounds capable of neutralizing the transesterification catalyst, for example, sulfur-containing acid compounds or derivatives formed therefrom. The compound capable of neutralizing the transesterification

catalyst may be used in an amount of usually 0.5 to 10 equivalents and preferably 1 to 5 equivalents on the basis of 1 equivalent of the alkali metal contained in the catalyst. Further, the compound capable of neutralizing the transesterification catalyst may be used in an amount of usually 1 to 100 ppm and preferably 1 to 20 ppm on the basis of the polycarbonates.

[0039]

The viscosity-average molecular weight of the aromatic polycarbonate resin is not particularly limited, and is usually not less than 10,000 and preferably not less than 15,000. Meanwhile, the viscosity-average molecular weight as used therein means the value obtained by the following method. That is, using an Ubbelohde viscometer, the intrinsic viscosity [η] of a solution of an aromatic polycarbonate resin sample in methylene chloride is measured at 20°C, and the viscosity-average molecular weight was calculated according to the following formulae (1) and (2):

[0040]

$$\eta_{sp}/C = [\eta] \times (1 + 0.28\eta_{sp}) \qquad (1)$$

$$[\eta] = 1.23 \times 10^{-4} \times (Mv)^{0.83} \qquad (2)$$

In the formula (2), η_{sp} is an intrinsic viscosity [η] of a solution of an aromatic polycarbonate resin sample in methylene chloride as measured at 20°C; and C is a concentration of the methylene chloride solution, wherein

the methylene chloride solution used has a concentration of the aromatic polycarbonate resin sample of 0.6 g/dL.

[0041]

[First invention]

The first invention is characterized in that when treating the thus produced aromatic polycarbonate resin with a polymer filter, a filter in which a concentration ratio of a chromium atom to an iron atom (Cr/Fe) which are present on an outermost surface thereof as measured by X-ray photoelectron spectroscopy is not less than 1.5 is used as the polymer filter.

[0042]

The polymer filter is a filter serving for removing foreign matters present in the aromatic polycarbonate resin by passing the resin therethrough. The configuration of the polymer filter usable in the present invention may be generally of any known type such as a candle type, a pleat type and a leaf disk type. Among these filters, especially preferred is a leaf disk-type polymer filter. The leaf disk-type polymer filter usually has a circular disk shape and is constructed from one or more layers obtained by using one or more woven wire nettings having various wire diameters and numerical apertures. The weaving of the polymer filter may be a plain weave, a twilled weave, a plain Dutch (tatami) weave, a twilled Dutch weave, etc. The

polymer filter may also be in the form of a nonwoven fabric. The material of the polymer filter is usually a stainless steel-based material such as SUS-316 and SUS-316L, and the polymer filter may also be formed from sintered metal or a resin. In addition, the absolute filtering accuracy of the polymer filter is usually 0.5 to 50 μm and preferably 0.5 to 20 μm.

[0043]

The X-ray photoelectron spectroscopy (ESCA) is a method for detecting photoelectrons driven out of a sample by photoelectric effect. Since the depth of escape of the photoelectrons is as shallow as about 50 Å, the element composition measurable by ESCA is only a composition in a region of the sample extending up to several tens Å from an outermost surface thereof.

[0044]

In commercially available polymer filters, a concentration ratio of a chromium atom to an iron atom (Cr/Fe) as measured on an outermost surface thereof upon purchase (before use) is not more than about 0.3. In order to enhance the concentration ratio up to not less than 1.5, the polymer filters may be washed, for example, with nitric acid to dissolve iron as a base component with the acid, thereby increasing a proportion of Cr therein.

[0045]

In the present invention, when regenerating the polymer filter already used, the above-mentioned modification procedure may be conducted. More specifically, the polymer filter that is deteriorated in filterability due to increased pressure loss is dismounted from a melting extruder and then subjected to regeneration treatment. In this case, the polymer filter is washed with nitric acid to conduct the above surface modification.

[0046]

The regeneration treatment (heat treatment) of the polymer filter includes a roasting treatment for removing organic substances deposited thereon, followed by the above washing treatment with nitric acid. The atmosphere of the roasting treatment may be generally a water vapor atmosphere and/or an oxygen atmosphere. The roasting time is usually 3 to 200 hr and preferably 5 to 100 hr. The roasting temperature is usually 260 to 480°C and preferably 300 to 450°C.

[0047]

The surface of the thus roasted polymer filter is usually stained. In the polymer filter used in the present invention, the thickness of a carbon film layer on an outermost surface thereof is preferably not more than 10 nm, and the thickness of an oxide film layer in a depth direction thereof is preferably not less than 100 nm, as

measured by Auger electron spectroscopy (AES). AES is a method for detecting Auger electrons generated upon irradiating an electron beam to the sample to measure kinds and amounts of elements present on the surface of the sample. For example, AES is known as a method for conducting analysis in depth direction using sputtering method in which distribution of a specific element in depth direction is measured while sputtering.

[0048]

In the present invention, the washing treatment with nitric acid is conducted after the above roasting treatment. It is not necessary to conduct a bright treatment as a washing treatment with an acid such as oxalic acid and citric acid prior to the roasting treatment. The washing treatment with nitric acid is usually conducted by sufficiently contacting the polymer filter with nitric acid which generally conducted by an immersion method or a solution flowing method. The concentration of nitric acid is usually 5 to 50% by weight and preferably 10 to 30% by weight. The temperature of the solution when immersing the polymer filter therein or flowing the solution through the polymer filter is usually 5 to 100°C and preferably 50 to 90°C. The immersion time is usually 5 to 120 min and preferably 10 to 60 min.

[0049]

When conducting the above washing treatment with nitric acid, the concentration ratio of a chromium atom to an iron atom (Cr/Fe) on an outermost surface of the filter is increased to not less than 1.5 and preferably not less than 1.8. By using the polymer filter having such surface properties, the resin to be filtered can be prevented from suffering from prolonged retention and deterioration thereof in the filter, and the catalytic action of constituent metals in the filter can be suppressed. The reason therefor is considered as follows though not clearly determined. That is, it is suggested that the catalytic action is suppressed owing to immobilization of the filter by the washing treatment with nitric acid. Meanwhile, the upper limit of frequency of the regeneration treatment for the polymer filter is about 20 times from the viewpoints of strength of the polymer filter, etc. When subjecting the polymer filter to such a repeated regeneration treatment, the concentration ratio of a chromium atom to an iron atom (Cr/Fe) on an outermost surface thereof is about 5.

[0050]

In accordance with the present invention, it is possible to produce an aromatic polycarbonate resin which is reduced in the number of foreign matters such as burnings and fisheyes and content of phenols. The aromatic polycarbonate resin of the present invention may also

comprise conventionally known additives according to the aimed applications thereof. Examples of the additives include other thermoplastic resins, flame retardants, impact modifiers, antistatic agents, slip agents, anti-blocking agents, lubricants, antifogging agents, natural oils, synthetic oils, waxes, organic fillers and inorganic fillers. The purified aromatic polycarbonate resin produced by the process of the present invention may be used as mechanical parts, parts of electric devices, haberdasheries, as well as films, sheets and bottles.

[0051]

The present invention relates to a process for producing a purified aromatic polycarbonate resin which is characterized by using a polymer filter which is modified to show specific conditions. As described above, the polymer filter is modified by regenerating the filter. Therefore, from such a viewpoint, as described in the present specification, the present invention also involves, as an alternative invention, the process for producing a purified aromatic polycarbonate resin by treating a molten aromatic polycarbonate resin with the polymer filter which is characterized by including a regenerating treatment for regenerating the polymer filter showing a deteriorated filtering performance in which the polymer filter is sequentially subjected to roasting treatment and washing

treatment with nitric acid without conducting any bright treatment, and the washing treatment with nitric acid is repeated after every regeneration treatment, whereby the concentration ratio of a chromium atom to an iron atom (Cr/Fe) on an outermost surface of the filter is controlled to not less than 1.5.

[0052]

For reference, the change in modified condition of the polymer filter in the above respective treatments is shown below in Table 1. The conditions of the respective treatments shown in Table 1 are as follows. In addition, the measurement conditions for ESCA and AES are described hereinafter.

[0053]

<Nitric acid treatment>

The polymer filter is immersed in 30 wt% nitric acid (30°C) for 30 min.

<Roasting treatment>

The polymer filter is heat-treated in a water vapor atmosphere at 310°C for 40 hr, and then further heat-treated in an oxygen atmosphere at 420°C for 52 hr.

<Bright treatment>

The polymer filter is immersed in an aqueous solution having an oxalic acid concentration of 5% by weight and a citric acid concentration of 5% by weight (80°C) for 1 hr.

[0054]

Table 1

Reference Examples	Nitric acid treatment	Roasting	Bright treatment
Reference Example 1	None	None	None
Reference Example 2	Conducted	None	None
Reference Example 3	Conducted	Conducted	None
Reference Example 4	Conducted	Conducted	Conducted

Table 1 (continued)

Reference Examples	ESCA	AES	
	Cr/Fe	Thickness of carbon film layer (nm)	Thickness of oxygen film layer (nm)
Reference Example 1	0.3	19	16
Reference Example 2	0.9	13	41
Reference Example 3	0.1	13	190
Reference Example 4	0.5	7	195

[Second and third inventions]

[0055]

The polymer filter used in the purification step for removing foreign matters from the aromatic polycarbonate resin, is preferably the same polymer filter as described in the first invention. Meanwhile, the melting extruder may be

usually in the form of a vented single- or multi-screw extruder. In particular, a meshing-type twin screw extruder is preferably used. The rotating directions of the screws in the extruder may be the same or different.

[0056]

The second invention relates to the process for producing polycarbonate resins in which after producing a polycarbonate resin A having a viscosity-average molecular weight Ma, production conditions are changed to produce a polycarbonate resin B having viscosity-average molecular weight Mb smaller than the viscosity-average molecular weight Ma using the same production facilities as used for production of the polycarbonate resin A. The viscosity-average molecular weight Ma is usually not less than 15,000, preferably not less than 20,000 and more preferably not less than 23,000. The upper limit of the viscosity-average molecular weight Ma is usually 100,000. The lower limit of the viscosity-average molecular weight Mb is usually 10,000, preferably 13,000 and more preferably less than 15,000. The difference between the viscosity-average molecular weight Ma and the viscosity-average molecular weight Mb is usually not less than 10,000, preferably not less than 2,000 and more preferably not less than 3,000.

[0057]

Also, the third invention relates to the process for

producing polycarbonate resins in which after producing a polycarbonate resin C having a branching degree Nc, production conditions are changed to produce a polycarbonate resin D having a branching degree Nd smaller than the branching degree Nc using the same production facilities as used for production of the polycarbonate resin C. The branching degree Nc is usually 0.2 to 1 mol%, preferably 0.3 to 1 mol% and more preferably 0.4 to 1 mol%. The branching degree Nd is usually 0.05 to 0.5 mol%, preferably 0.1 to 0.5 mol% and more preferably 0.2 to 0.5 mol%. The difference between the branching degree Nc and the branching degree Nd is usually not less than 0.01 mol%, preferably not less than 0.05 mol% and more preferably not less than 0.10 mol%.

[0058]

The switching between these operations may be conducted by the same method as described in the above Japanese Patent Application Laid-open (KOKAI) No. 2-153925(1990), i.e., by changing reaction conditions such as catalyst concentration, polycondensation temperature and residence time in the reactor. In the process for producing an aromatic polycarbonate resin by transesterification method, it is difficult to completely avoid formation of branched structural units upon polycondensation. In particular, when producing the product of such a grade having a large viscosity-average molecular weight (Mv), the

polycondensation temperature or catalyst concentration must be necessarily increased, thereby causing such a tendency that the number of fisheyes which will be derived from the branched structural units is increased.

[0059]

In addition, when the polymer filter to be mounted to the melting extruder is selected according to the viscosity-average molecular weight (Mv) of the polycarbonate resin produced, the polymer filter having a larger mesh size (opening diameter) is used for producing the polycarbonate resin A, whereas the polymer filter having a smaller mesh size is used for producing the polycarbonate resin B. When switching the operation of the process from production of the polycarbonate resin A to production of the polycarbonate resin B, the polymer filter having a larger mesh size is changed over to that having a smaller mesh size, and the difference between the number of fisheyes in the resin as measured 2 hr before changing over the polymer filters and that as measured 1 hr before changing over the polymer filters is not more than 10. The reason why the polymer filter having a larger mesh size is used when producing the polycarbonate resin having a large Mv is that excessive increase in pressure loss depending upon viscosity which might be caused in exchange for slight deterioration in removal rate of foreign matters when using the polymer

filter having a smaller mesh size should be prevented to thereby avoid occurrence of breaking of the polymer filter. Meanwhile, the above mesh sizes are each a relative size, and the mesh sizes of the polymer filters actually used may be determined according to quality of the aimed resin (such as content of fisheyes therein).

[0060]

On the other hand, when the polymer filter to be mounted to the melting extruder is selected according to a branching degree of the polycarbonate resin treated therewith, a polymer filter having a larger mesh size is used as the polymer filter upon producing the polycarbonate resin C, whereas a polymer filter having a smaller mesh size is used as the polymer filter upon producing the polycarbonate resin D. When the operation of the process is switched from production of the polycarbonate resin C to production of the polycarbonate resin D, the polymer filter having a larger mesh size is changed over to that having a smaller mesh size, and the difference between the number of fisheyes in the resin as measured 2 hr before changing over the polymer filters and that as measured 1 hr before changing over the polymer filters is controlled to not more than 10. The reason therefor is that the melt viscosity of a resin having a large branching degree becomes larger than that of a resin having a small branching degree in a low

shear rate range so that the same phenomenon observed when the Mv is large tends to be caused.

[0061]

The present invention is characterized in that when the operation of the process is switched from production of a product having a large viscosity-average molecular weight to production of a product having a small viscosity-average molecular weight or from production of a product having a large branching degree to production of a product having a small branching degree, the change-over from the polymer filter having a larger mesh size to that having a smaller mesh size is not conducted immediately after changing the reaction conditions, but the number of fisheyes in the aromatic polycarbonate resin passed through the polymer filter is continuously traced or monitored as described above, and the change-over to the polymer filter having a smaller mesh size is performed based on the change in the number of fisheyes thus traced or monitored.

[0062]

Upon switching the operation of the process from production of the product having a large average-viscosity molecular weight (Mv) to production of the product having a small average-viscosity molecular weight (Mv), when the polymer filter having a larger mesh size is changed over to that having a smaller mesh size immediately after changing

the reaction conditions, the following problems tend to be caused. That is, when the reaction conditions are changed, although the Mv of the aromatic polycarbonate resin in the reaction system is reduced (i.e., the viscosity of the obtained resin is lowered) in a relatively early stage, the condition of the increase in the number of fisheyes in the resin which is observed upon producing the product having a large Mv before changing the reaction conditions is still continued for a while, and then gradually dissipated, whereby the reaction system is returned to a steady state. Therefore, if the polymer filter is changed over to that having a smaller mesh size immediately after changing the reaction conditions, filtration of such a resin may become difficult, so that the aromatic polycarbonate resin comprising impurities tends to be discharged from the polymer filter for a long period of time.

[0063]

On the contrary, when the polymer filter having a larger mesh size is continuously used even after changing the reaction conditions as described above, since the Mv of the aromatic polycarbonate resin in the reaction system is reduced (i.e., the viscosity is lowered), so that filtration of the aromatic polycarbonate resin comprising impurities is promoted.

[0064]

Also, upon switching the operation of the process from production of the product having a large branching degree to production of the product having a small branching degree, when the polymer filter having a larger mesh size is changed over to that having a smaller mesh size immediately after changing the reaction conditions, the following problems tend to be caused. That is, when the reaction conditions are changed, although the branching degree of the aromatic polycarbonate resin in the reaction system is reduced in a relatively early stage, the condition of the increase in the number of fisheyes in the resin which is observed upon producing the product having a large branching degree before changing the reaction conditions is still continued for a while, and then gradually dissipated, whereby the reaction system is returned to a steady state. Therefore, if the polymer filter is changed over to that having a smaller mesh size immediately after changing the reaction conditions, filtration of such a resin may become difficult, so that the aromatic polycarbonate resin comprising impurities tends to be discharged from the polymer filter for a long period of time.

[0065]

On the contrary, when the polymer filter having a larger mesh size is continuously used even after changing the reaction conditions as described above, since the

branching degree of the aromatic polycarbonate resin in the reaction system is reduced, so that filtration of the aromatic polycarbonate resin comprising impurities is promoted.

[0066]

Thus, in the present invention, upon switching the operation of the process from production of the product having a large viscosity-average molecular weight (Mv) or a large branching degree to production of the product having a small viscosity-average molecular weight (Mv) or a small branching degree, the polymer filter having a larger mesh size is still continuously used for a while even after changing the reaction conditions. However, if such a condition is maintained for an excessively long time, the removal rate of impurities is kept in a low level, so that the reaction system is hardly controlled to a steady state for obtaining the product having a small Mv or a small branching degree.

[0067]

For this reason, in the present invention, the number of fisheyes in the aromatic polycarbonate resin passed through the polymer filter is traced or monitored, and the polymer filter is changed over to that having a smaller mesh size on the basis of the change in the number of fisheyes thus traced or monitored. After changing the reaction

conditions, the process is shifted as follows. That is, the melt viscosity of the resulting aromatic polycarbonate resin is lowered, the pressure loss of the melting extruder is reduced, and the number of fisheyes in the aromatic polycarbonate resin passed through the polymer filter is gradually decreased and then reaches an approximately constant value.

[0068]

In the present invention, the time at which the variation in the number of fisheyes is reduced and the number of fisheyes reaches an approximately constant value can be used as the time of change-over between the polymer filters. Alternatively, the change-over between the polymer filters may be determined based on previously stored data showing the shift of the number of fisheyes. The change-over between the polymer filters may be conducted according to an ordinary method by temporarily stopping supply of the resin from the melting extruder. The phrase "variation in the number of fisheyes is reduced and the number of fisheyes reaches an approximately constant value" as used herein means that when the number of fisheyes is measured with the passage of time, the difference between the number of fisheyes as measured before 1 hr and that as measured at the present time is not more than 10.

[0069]

According to the present invention, upon producing the aromatic polycarbonate resins of different grades which are different in viscosity-average molecular weight (Mv) or branching degree from each other, it is possible to produce the aromatic polycarbonate resins having a less number of fisheyes and exhibiting an excellent hue in an efficient manner.

[0070]

The aromatic polycarbonate resins obtained in the above respective inventions may also comprise conventionally known additives according to the requirements. As the additives, there may be used, for example, those additives appropriately selected from other thermoplastic resins, flame retardants, impact modifiers, antistatic agents, slip agents, anti-blocking agents, lubricants, anti-fogging agents, natural oils, synthetic oils, waxes, organic fillers and inorganic fillers. The aromatic polycarbonate resins produced by the process of the present invention may be used as mechanical parts, parts of electric devices or appliances, sundries, as well as films, sheets and bottles.

EXAMPLES

[0071]

The present invention is described in more detail below by the following Examples. However, these Examples are only

illustrative and not intended to limit a scope of the present invention. The respective properties were measured by the following methods.

[0072]

(1) X-ray photoelectron spectroscopy (ESCA)

A filter material portion (fibrous portion) of the polymer filter was cut to form a sample having a size of 1 cm square, and a concentration ratio of a chromium atom to an iron atom on an outermost surface of the sample was measured using "Quantum 2000" manufactured by PHI Corp. Using a monochromatized AlK α-ray as an excited X-ray source, a 20 μmϕ beam of the X-ray was irradiated near a central portion of the fibrous sample. The spectrum of energy of electrons discharged from the surface of the sample upon irradiation with the X-ray was measured under the following conditions: sampling angle: 45°; energy passing through an inside of spectroscope: 58.7 eV. The respective photoelectron peaks: C1s, O1s, Cr2p, Fe2p and Ni2p observed on the spectrum were subjected to background subtraction treatment to calculate integrated intensities thereof which were then converted into atomic concentrations by using a sensitivity correction coefficient appended to the apparatus.

[0073]

(2) Auger electron spectroscopy (AES)

The analysis of an oxide film layer of the filter in

its depth direction by AES method was conducted using "JAMP-7800" manufactured by Nippon Denshi Co., Ltd., under the following measuring conditions. In the AES measurement, an electron beam (acceleration voltage: 10 kV; sample current: 1.7×10^{-8} A; probe diameter: about 1 μm) was irradiated to the surface of the sample to measure a peak intensity of Auger electrons discharged therefrom. The peak intensities of the respective elements were converted into atomic concentrations by using a sensitivity correction coefficient appended to the apparatus. The ion sputtering was conducted using an Ar ion gun to irradiate an "Ar + ion" beam accelerated at 1 keV to the surface of the sample. The Ar ion sputtering and the AES measurement was alternately repeated to continuously trace or monitor the change in elemental composition of the sample, so that the thickness of a portion at which an oxygen concentration was reduced up to half of the oxygen concentration on the surface of the sample was determined as "thickness of oxide film layer" whereas the thickness of a portion at which a carbon concentration was reduced up to half of the carbon concentration on the surface of the sample was determined as "thickness of carbon film layer". In this case, the respective thicknesses were calculated in terms of a depth of SiO_2.

[0074]

(3) Number of fisheyes (F/E):

The resulting aromatic polycarbonate resin pellets were dried at 130°C for 5 hr and then subjected to extrusion molding at 320°C to obtain a film having a width of 140 mm and a thickness of 70 μm. The extrusion molding was conducted using a 30 mmϕ single-screw extruder manufactured by Isuzu Kako Co., Ltd. Next, using an optical foreign material inspection apparatus "GX40K" manufactured by Dia Instruments Co., Ltd., the number of fisheyes (size: 50 to 500 μm) in a portion of the film (volume: 952 cm^3) having a width of 80 mm (selected from a central portion of the film), a length of 1.7 m and a thickness of 70 μm was measured. More specifically, in the case where light irradiated to the sample is used in an amount of 800 mV, the number of fisheyes as measured when the amount of light absorbed therein is in the range of 100 to 300 mV is expressed by (A), whereas the number of fisheyes as measured when the amount of light absorbed therein is in the range of more than 300 mV is expressed by (B). The number of fisheyes is calculated according to the following formula (1):

[0075]

Number of fisheyes = (A) - (B) (1).

The measurement was repeated twice, and the number of fisheyes was determined as an average value of the values obtained from the measurements.

[0076]

(4) Amount of residual monomers

A solution prepared by dissolving 1.2 g of the thus obtained aromatic polycarbonate resin pellets in 7 mL of methylene chloride was mixed with 23 mL of acetone while stirring to re-precipitate the aromatic polycarbonate resin. The resulting supernatant was measured by liquid chromatography ["LC-10AT" manufactured by Shimadzu Seisakusho Co., Ltd.; column: "MCI GEL ODS" (pore size of gel: 5 μm); 4.6 mm ID x 150 mm L; detector: UV 219 nm; eluent: acetonitrile/water = 4/6 (volume ratio)] to quantitatively determine amounts of residual phenol, residual bisphenol A (BPA) and residual diphenyl carbonate (DPC) in the resin.

[0077]

(5) Hue

The obtained aromatic polycarbonate resin pellets were dried at 120°C for 5 hr, and then molded using an injection molding machine "J100SS-2" manufactured by Nippon Seikosho Co., Ltd., at a barrel temperature of 300°C and a mold temperature of 90°C, thereby obtaining a sheet having a thickness of 3 mm and a size of 100 mm square. The hue of the sheet was observed by naked eyes and evaluated.

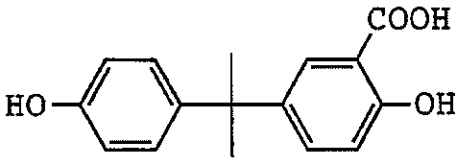
[0078]

(6) Branching degree

The branching degree was expressed by a ratio (mol%) of total moles of branched compounds represented by the following formulae (1) to (5) based on 1 mole of bisphenol A constitutional unit. More specifically, the contents of the respective compounds were determined as follows. That is, 1 g of aromatic polycarbonate (sample) was dissolved in 100 mL of methylene chloride, and then 18 mL of a 28% methanol solution of sodium methoxide and 80 mL of methanol were added to the resulting solution. Further, after adding 25 mL of pure water to the solution, the obtained mixture was stirred at room temperature for 2 hr to completely hydrolyze the sample. Thereafter, the resulting solution was neutralized by adding 1N hydrochloric acid thereto to separate the methylene chloride layer therefrom, thereby obtaining a hydrolyzate. Then, 0.05 g of the hydrolyzate was dissolved in 10 mL of acetonitrile, and the resulting solution was measured using a reversed phase high-pressure liquid chromatography (HPLC). In the reversed phase high-pressure liquid chromatography, using a mixed solvent comprising acetonitrile and a 10 mM ammonium acetate aqueous solution as an eluent, the measurement was conducted at a column temperature of 40°C under the condition that the mixing ratio of acetonitrile to the 10 mM ammonium acetate aqueous solution varied with a gradient of from 20/80 at start of the measurement up to 80/20. In the measurement, a

UV detector "SPD-6A" (detection UV wavelength: 280 nm) manufactured by Shimadzu Seisakusho Co., Ltd., was used. The branched compounds represented by the following formulae (1) to (5) were respectively identified using a LC-MS "Agilent-1100" manufactured by Agilient Co., Ltd., and a NMR "AL-400" manufactured by Nippon Denshi Co., Ltd. The contents of the respective compounds were calculated from peak areas of the compounds relative to a peak area of bisphenol A based on a calibration curve of bisphenol A previously prepared.

[0079]



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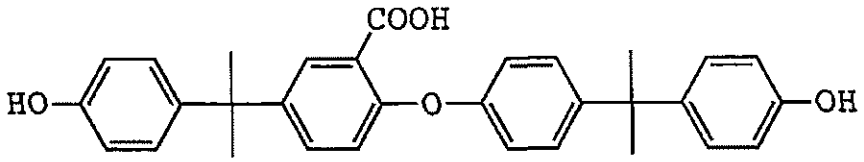

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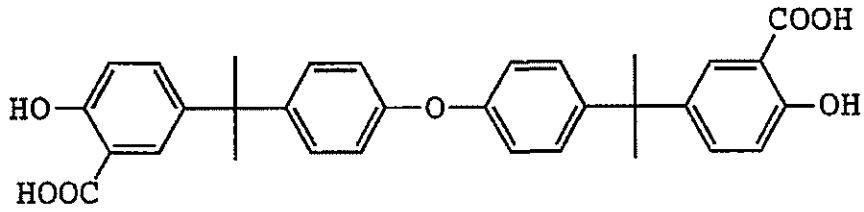

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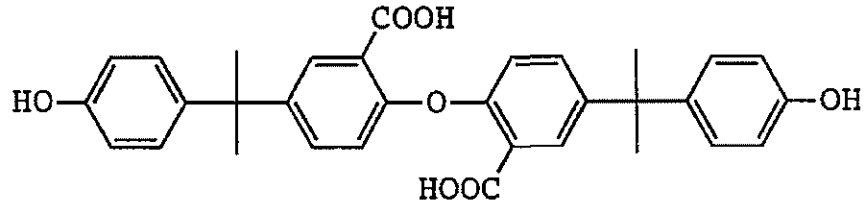

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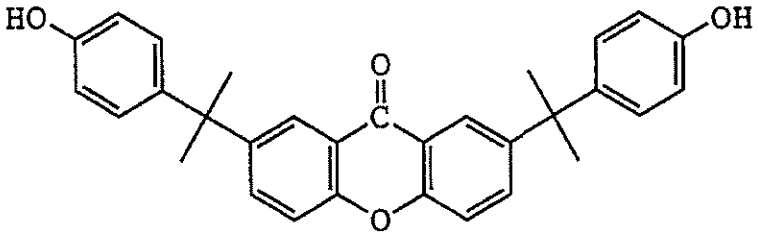

(5)

[0080]

[Example and Comparative Example relating to the first invention]

Comparative Example 1A and Example 1A:

Using a production facility mainly constituted from first to fourth reactors (all vertical stirring reactors), a fifth reactor (horizontal stirring reactor) and a twin-screw melting extruder (screw diameter: 0.046 m; L/D = 36) fitted

at an outlet thereof with a polymer filter, aromatic polycarbonate resins of two different grades having viscosity-average molecular weights (Mv) of about 25,500 and about 21,000, respectively, were alternately produced every 1 month by ordinary transesterification method. The polymer filter used was a commercially available leaf disk-type polymer filter (manufactured by Nagase Sangyo Co., Ltd.; metallic nonwoven fabric type having an absolute filtering accuracy of 50 μm (material: SUS316L)) comprising 90 leaf disks fitted to a center post (hereinafter referred to merely as "P/F"). Before being used, the P/F was washed with a nitric acid (immersed in 30 wt% nitric acid (30°C) for 30 min), and then washed with water and dried. The P/F had a concentration ratio of a chromium atom to an iron atom (Cr/Fe) of 0.9 as measured on an outermost surface thereof, a thickness of a carbon film layer of 13 nm as measured on the outermost surface thereof, and a thickness of an oxide film layer of 41 nm as measured in a depth direction thereof.

[0081]

The change-over between the polymer filters (P/F) of different grades was made every switching operation of the production process between products of different grades. Before reused, the respective P/F was subjected to regeneration treatment including the following procedures: (1) roasting the filter (heat-treating the filter at 310°C

for 40 hr in a water vapor atmosphere, and then heat-treating the filter at 420°C for 52 hr in an oxygen atmosphere); (2) washing the filter with nitric acid (immersing the filter in 30 wt% nitric acid (30°C) for 30 min); and (3) washing the filter with water, followed by drying.

[0082]

The P/F for the branched grade was analyzed by X-ray photoelectron spectroscopy and Auger electron spectroscopy according to the above-mentioned methods (1) and (2) to determine a composition of the surface thereof. In addition, the number of fisheyes, amounts of residual monomers and hue of the resulting aromatic polycarbonate resin pellets were measured every time upon changing-over the P/F according to the above-mentioned methods (3) to (5). The results are shown in Table 2. Meanwhile, in Table 2, all the measured values of ESC and AES for the P/F mean the values obtained upon initiation of respective use periods of the P/F. For example, the numeral value "1.4" appearing in the column "Cr/Fe" of Table 2 means the value obtained by measuring the ratio Cr/Fe of the P/F which has been subjected to the above regeneration treatment after used for 1 month, before starting the 3rd month period (from initiation of switching of the operation) of use of the P/F. Also, the number of fisheyes, amounts of residual monomers and hue of the

resulting aromatic polycarbonate resin pellets were measured every 8 hr over 2 days from immediately after switching the operation. The numerical values shown in Table 2 are each an average value calculated from these measured values.

[0083]

Table 2

<Data for branched grade>

Elapsed period from initiation of switching the operation	ESCA	AES		Number of F/E
	Cr/Fe	Thickness of carbon film layer (nm)	Thickness of oxygen film layer (nm)	
1 month*	0.9	13	41	4890
3 months**	1.4	11	82	1694
5 months	1.8	6	163	211
7 months	2.2	7	460	153
9 months	3.3	5	1083	147

Table 2 (continued)

Elapsed period from initiation of switching the operation	Amounts of residual monomers			Hue
	PhOH	BPA	DPC	
1 month*	78	38	72	Reddish
3 months**	66	34	61	Reddish
5 months	33	37	44	Transparent
7 months	34	36	48	Transparent
9 months	33	32	45	Transparent

Note *, **: The "one month" and "three months" in Table 2 correspond to the respective Comparative Examples.

[0084]

[Examples and Comparative Examples relating to the second and third inventions]

[0085]

Example 1B:

Diphenyl carbonate (DPC) and bisphenol A (BPA) were mixed with each other at a predetermined molar ratio (DPC/BPA = 1.050) in a nitrogen gas atmosphere to prepare a raw material melt solution. The thus prepared raw material melt solution was continuously fed to the first vertical stirring reactor having a capacity of 100 L which was controlled to a temperature of 220°C and a pressure of 1.33×10^4 Pa through a raw material inlet tube at a flow rate of 88.7 kg/hr. The opening degree of a valve provided on a polymer discharge line connected to a bottom of the reactor was controlled such that the residence time in the first reactor was 60 min, thereby keeping a liquid level in the reactor constant. Simultaneously with initiating feed of the raw material melt solution, a cesium carbonate aqueous solution as a catalyst was continuously fed to the first reactor at a feed rate of 1.0 μmol per 1 mol of bisphenol A (2.0 μmol in terms of metallic cesium per 1 mol of bisphenol A).

[0086]

The reaction solution withdrawn from the bottom of the reactor was successively and sequentially fed to the second and third vertical stirring reactors (each having a capacity of 100 L) and then to the fourth horizontal stirring reactor

(capacity: 150 L) in a continuous manner, and the obtained polymer was withdrawn from a polymer discharge port provided on a bottom of the fourth reactor. Next, the resulting polymer was introduced while kept in a molten state to a twin-screw extruder (screw diameter: 0.046 m; L/D = 36) fitted at a die outlet thereof with a polymer filter, and continuously kneaded with butyl p-toluenesulfonate (in an amount of 4 mol based on 1 mol of cesium carbonate used as the catalyst), and the resulting kneaded material was extruded into strands through the die and cut using a cutter, thereby obtaining aromatic polycarbonate resin pellets of a high-molecular weight grade (Mv: 25,500).

[0087]

The reaction conditions of the second to fourth reactors were respectively controlled such that the second reactor was operated under the conditions of 240°C, 2.00 x 10^3 Pa and 75 rpm; the third reactor was operated under the conditions of 270°C, 66.7 Pa and 75 rpm; and the fourth reactor was operated under the conditions of 290°C, 67 Pa and 5 rpm. These reaction conditions were shifted to higher temperature, higher vacuum and lower stirring speed as the reaction proceeded. In addition, during the reaction, the liquid levels in the respective reactors were controlled such that the residence time in the second and third reactors was 60 min, and the residence time in the fourth

reactor was 90 min, while simultaneously distilling off phenols by produced.

[0088]

The polymer filter used above was a commercially available leaf disk-type polymer filter (manufactured by Nagase Sangyo Co., Ltd.; metallic nonwoven fabric type having an absolute filtering accuracy of 50 μm (material: SUS316L)) comprising 90 leaf disks fitted on a center post (hereinafter referred to merely as a "polymer filter A").

[0089]

The above operation was continued for one month, and then the molar ratio of DPC/BPA was gradually increased until reaching 1.090 at which time the amount of the cesium carbonate aqueous solution fed was reduced to one half, and the temperature of the fourth reactor was decreased, thereby changing the production conditions to those for producing a low-molecular weight grade (Mv: 15,000).

[0090]

The number of fisheyes in the aromatic polycarbonate resin passed through the polymer filter (A) was traced and measured every one hour. After 1 hr from the time at which the number of fisheyes was kept approximately at a predetermined constant value (140) (the elapsed time of 18 hr after changing the reaction conditions), the change-over between the polymer filters was performed, and production of

pellets of the aromatic polycarbonate resin having a low-molecular weight grade (Mv: 15,000) was continued. The polymer filter used for production of the low-molecular weight grade was a commercially available leaf disk-type polymer filter (manufactured by Nippon Pole Co., Ltd.; metallic nonwoven fabric type having an absolute filtering accuracy of 10 μm (material: SUS316L)) comprising 120 leaf disks fitted on a center post (hereinafter referred to merely as a "polymer filter B"). Properties of the aromatic polycarbonate resin passed through the polymer filter (B) were measured. As a result, it was confirmed that the obtained aromatic polycarbonate resin had a viscosity-average molecular weight (Mv) of 15,100, and the number of fisheyes therein was 24 and the hue thereof was transparent.

[0091]

Comparative Example 1B:

The same procedure as defined in Example 1B was conducted except that after producing pellets of the aromatic polycarbonate resin having a high-molecular weight grade, the production conditions were changed to those for production of the low-molecular weight grade, and simultaneously the polymer filter (A) was changed-over to the polymer filter (B), thereby obtaining aromatic polycarbonate resins. As a result, it was confirmed that it took 92 hr after changing the reaction conditions until

properties of the aromatic polycarbonate resin passed through the polymer filter (B) became approximately identical to those of the aromatic polycarbonate resin obtained in Example 1B (Mv: 15,000; number of fisheyes: 33).

[0092]

Example 2B:

Separately, in the same manner as in Example 1B, the operation for production of the aromatic polycarbonate resin having a high-molecular weight grade (high branching degree grade) (branching degree: 0.48 mol%) was continued for one month. Thereafter, the production conditions were changed such that the amount of the cesium carbonate aqueous solution fed was reduced to one half, and the residence time in the fourth reactor was 120 min, thereby producing a low branching degree grade (branching degree: 0.27 mol%; Mv: 25,600).

[0093]

The number of fisheyes in the aromatic polycarbonate resin passed through the polymer filter (A) was traced and measured every one hour. After 1 hr from the time at which the number of fisheyes was kept approximately at a predetermined constant value (427) (the elapsed time of 11 hr after changing the reaction conditions), the change-over between the polymer filters was performed, and production of pellets of the aromatic polycarbonate resin having a low-

branching degree grade (branching degree: 0.27 mol%) was continued. The polymer filter used for production of the low-branching degree grade was a commercially available leaf disk-type polymer filter (manufactured by Nagase Sangyo Co., Ltd.; metallic nonwoven fabric type having an absolute filtering accuracy of 20 μm (material: SUS316L)) comprising 90 leaf disks fitted on a center post (hereinafter referred to merely as a "polymer filter B'"). Properties of the aromatic polycarbonate resin passed through the polymer filter (B') were measured. As a result, it was confirmed that the obtained aromatic polycarbonate resin had a viscosity-average molecular weight (Mv) of 25,500 and a branching degree of 0.27 mol%, and the number of fisheyes therein was 255 and the hue thereof was transparent.

[0094]

Comparative Example 2B:

The same procedure as defined in Example 2B was conducted except that after producing pellets of the aromatic polycarbonate resin having a high branching degree grade, the production conditions were changed to those for production of the low branching degree grade, and simultaneously the polymer filter (A) was changed-over to the polymer filter (B'), thereby obtaining aromatic polycarbonate resins. In this case, it was confirmed that it took 52 hr after changing the reaction conditions until

properties of the aromatic polycarbonate resin passed through the polymer filter (B') became approximately identical to those of the aromatic polycarbonate resin obtained in Example 2B (Mv: 25,600; number of fisheyes: 263).

CLAIMS

1. A process for producing aromatic polycarbonate resins in which after producing a polycarbonate resin A having a viscosity-average molecular weight Ma, production conditions are changed to produce a polycarbonate resin B having a viscosity-average molecular weight Mb smaller than the viscosity-average molecular weight Ma using the same production facilities as used for production of the polycarbonate resin A, said process comprising at least a polycondensation step of conducting transesterification reaction of an aromatic dihydroxy compound with a carbonic diester compound and a purification step of allowing the resulting molten aromatic polycarbonate resin to pass through a polymer filter using a melting extruder to remove foreign matters therefrom, wherein a filter having a larger mesh size (opening diameter) is used as the polymer filter when producing the polycarbonate resin A, and a filter having a smaller mesh size (opening diameter) is used as the polymer filter when producing the polycarbonate resin B; when switching operation of the process from production of the polycarbonate resin A to production of the polycarbonate resin B, the polymer filter having a larger mesh size is changed over to the polymer filter having a smaller mesh size; and a difference between the number of fisheyes in the

resin as measured 2 hr before changing over the polymer filters and that as measured 1 hr before changing over the polymer filters, is not more than 10.

2. A process for producing aromatic polycarbonate resins in which after producing a polycarbonate resin C having a branching degree Nc, production conditions are changed to produce a polycarbonate resin D having a branching degree Nd smaller than the branching degree Nc using the same production facilities as used for production of the polycarbonate resin C, said process comprising at least a polycondensation step of conducting transesterification reaction of an aromatic dihydroxy compound with a carbonic diester compound and a purification step of allowing the resulting molten aromatic polycarbonate resin to pass through a polymer filter using a melting extruder to remove foreign matters therefrom, wherein a filter having a larger mesh size (opening diameter) is used as the polymer filter when producing the polycarbonate resin C, and a filter having a smaller mesh size (opening diameter) is used as the polymer filter when producing the polycarbonate resin D; when switching operation of the process from production of the polycarbonate resin C to production of the polycarbonate resin D, the polymer filter having a larger mesh size is changed over to the polymer filter having a smaller mesh size; and a difference between the number of fisheyes in the

resin as measured 2 hr before changing over the polymer filters and that as measured 1 hr before changing over the polymer filters, is not more than 10.