

DESCRIPTION

METHOD FOR PRODUCING AROMATIC POLYCARBONATE RESIN COMPOSITION

5 TECHNICAL FIELD

The present invention relates to a method for producing an aromatic polycarbonate resin composition, more particularly to a method for producing an aromatic polycarbonate resin composition by an ester exchange reaction.

10 BACKGROUND ART

In recent years, aromatic polycarbonate resins are widely used in OA parts, automobile parts, building materials and so on, as engineering plastics excellent not only in mechanical properties such as impact resistance but also in heat resistance, transparency, and so on. In particular, they are widely used in applications to optical lenses and recording discs as optical materials, sheets and
15 bottles, while utilizing the properties such as impact resistance and transparency.

A method for producing the aromatic polycarbonate resin may be a so-called melt process conventionally known, which is a method of subjecting an aromatic diol and a carbonic diester to ester exchange in a molten state to continuously produce an aromatic polycarbonate resin while taking low-molecular-weight by-products such as phenol out of the system.

20 When the aromatic polycarbonate resin is used as a material, it is often used together with various types of thermal stabilizers added in order to maintain and improve its performance. These thermal stabilizers are normally mixed to be dispersed and uniformized in the aromatic polycarbonate by a kneading method using an extruder (cf. Patent Document 1).

Patent Document 1: JP-A-8-259687

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DISCLOSURE OF THE INVENTION

OBJECT TO BE ACCOMPLISHED BY THE INVENTION

Incidentally, for example, when the aromatic polycarbonate resin is produced by the melt process, the aromatic polycarbonate resin in a molten state and various types of additives such as a
30 thermal stabilizer are usually mixed in an extruder provided in the latter stage of a production line. Then, the aromatic polycarbonate resin extruded from the extruder is molded into pellets of predetermined size to become a product.

However, most of the additives added to the aromatic polycarbonate resin are in a powder or liquid state, and amounts thereof used are extremely small. Therefore, there is a problem that it is
35 often the case that when the aromatic polycarbonate resin and the additives are mixed in the extruder, the additives are not evenly distributed and uniformly mixed.

In this case, a conceivable method is such that they are added to the extruder in the form of a masterbatch preliminarily prepared from the additives and an appropriate polymer. However, when the masterbatch is prepared using a mixer such as a Henschel mixer, it is often the case that the
40 additives in the powder state are classified, so as to result in failure in achieving a uniform dispersion state. Furthermore, the additives in the liquid state might separate off after preparation of the masterbatch.

Furthermore, the above-mentioned melt process is generally a method for continuously producing the aromatic polycarbonate resin, and a transition product comes up, e.g., at switching of
45 products. Since the transition product is off standards, it is usually discarded as a loss of production.

However, it is not preferable to discard the loss of production from the viewpoint of a yield of products and saving of resources and it is desirable to effectively utilize the loss of production.

However, if the loss of production is recycled, thermal stability of the product might be deteriorated to reduce the value of product.

An object of the present invention is to provide a method for producing an aromatic polycarbonate resin composition with stable quality by uniformly mixing an additive such as a thermal stabilizer and an aromatic polycarbonate resin.

MEANS TO ACCOMPLISH THE OBJECT

In order to accomplish the object, the inventors of the present invention intensively and extensively studied, and, as a result, found that when aromatic polycarbonate pellets containing a thermal stabilizer are pneumatically transported through a branched pipe branched off from a pneumatic transport pipe, and are continuously supplied to the extruder in a state in which the thermal stabilizer is attached to the pellets, the above-mentioned loss of production can be effectively utilized and the effect on the quality can be minimized. The present invention has been accomplished based on the above finding.

Thus, the present invention provides a method for producing an aromatic polycarbonate resin composition containing a thermal stabilizer, the method comprising the following steps: a polycarbonate supply step of continuously supplying an aromatic polycarbonate in a molten state to an extruder; an extrusion step of mixing the aromatic polycarbonate supplied from the polycarbonate supply step with the thermal stabilizer in the extruder to obtain an aromatic polycarbonate mixture, and extruding the aromatic polycarbonate mixture from the extruder; a pellet formation step of pelletizing the aromatic polycarbonate mixture extruded from the extruder in the extrusion step, to form aromatic polycarbonate pellets; and a pellet recycle step of taking some of the aromatic polycarbonate pellets pelletized in the pellet formation step, continuously attaching the thermal stabilizer to the pellets, and continuously supplying the thermal stabilizer-attached pellets to the extruder into which the aromatic polycarbonate is supplied in the polycarbonate supply step.

Here, the production method of the aromatic polycarbonate resin composition to which the present invention is applied, is preferably configured so that it further comprises a pneumatic transport step of pneumatically transporting the aromatic polycarbonate pellets pelletized in the pellet formation step, through a transport pipe, and so that some of the aromatic polycarbonate pellets pelletized in the pellet formation step are pneumatically transported through a branched pipe branched off from the transport pipe.

Next, in the production method of the aromatic polycarbonate resin composition to which the present invention applied, the pellet recycle step is preferably a step wherein the thermal stabilizer attached to the aromatic polycarbonate pellets is in a liquid state. Here, the pellet recycle step is preferably a step wherein the thermal stabilizer attached to the aromatic polycarbonate pellets is an acidic compound or a derivative thereof. Furthermore, the thermal stabilizer is preferably a sulfonic acid or its ester which is in a liquid state and which may be substituted with a C₁₋₁₀ alkyl group.

Next, in the production method of the aromatic polycarbonate resin composition to which the present invention is applied, the pellet recycle step preferably comprises continuously attaching the thermal stabilizer to the aromatic polycarbonate pellets, in an amount of from 0.001 part to 1 part by weight to 100 parts by weight of the aromatic polycarbonate pellets.

Furthermore, the pellet recycle step preferably comprises supplying to the extruder the stabilizer-attached aromatic polycarbonate pellets in an amount of from 0.5 part to 5 parts by weight to 100 parts by weight of the aromatic polycarbonate to be supplied to the extruder.

Moreover, in the production method of the aromatic polycarbonate resin composition to which the present invention is applied, a viscosity average molecular weight (Mv₁) of the aromatic polycarbonate pelletized in the pellet formation step is preferably not more than a viscosity average molecular weight (Mv₂) of the aromatic polycarbonate in the molten state mixed with the thermal

stabilizer in the extruder in the extrusion step ($Mv_1 \leq Mv_2$).

Yet furthermore, the extrusion step preferably comprises mixing the thermal stabilizer in an amount of at most 0.002 part by weight to 100 parts by weight of the aromatic polycarbonate.

Moreover, the polycarbonate supply step preferably comprises obtaining the aromatic
 5 polycarbonate to be supplied to the extruder by a polycondensation reaction of an aromatic dihydroxy compound and a carbonic diester in the presence of a basic compound as a catalyst.

EFFECTS OF THE INVENTION

10 The present invention permits production of the aromatic polycarbonate resin composition with stable quality. In addition, the present invention improves the yield of the product by simple means and is expected to contribute to saving of resources.

BRIEF DESCRIPTION OF DRAWINGS

15 Fig. 1 is a drawing to show an example of a production apparatus of an aromatic polycarbonate resin composition.

Fig. 2 is a drawing to show an example of a production apparatus of an aromatic polycarbonate resin composition in which an additive such as a thermal stabilizer is attached using a plurality of blenders.

MEANINGS OF SYMBOLS

20 2a: First raw material preparation tank, 2b: Second raw material preparation tank, 3a, 3b: Anchor type stirring blade, 4a: Raw material supply pump, 5a: Catalyst supply port, 6a: First vertical reactor, 6b: Second vertical reactor, 6c: Third vertical reactor, 7a, 7b, 7c: MAXBLEND blade, 8a, 8b, 8c, 8d: Distillation pipe, 9a: Fourth horizontal reactor, 10a: Lattice type blade, 11a: Extruder, 12a, 12b, 12c: Additive supply line, 13a: Strand bath, 14a: Strand cutter, 15a: Sieve, 16a, 16b, 16c: Product silo,
 25 21a, 21b: Blender, 22a, 22b: Thermal stabilizer supply port, 81a, 81b, 81c, 81d: Condenser, 82a, 82b, 82c, 82d: Connecting pipe to depressurizer.

BEST MODE FOR CARRYING OUT THE INVENTION

30 The best mode for carrying out the invention (hereinafter, an embodiment of the invention) will be described in detail below. The present invention is not limited to the embodiment below, but can be carried out with various modifications within the scope of the invention. Furthermore, the drawings used are presented to explain the embodiment of the present invention, and do not show the actual sizes.

(POLYCARBONATE RESIN)

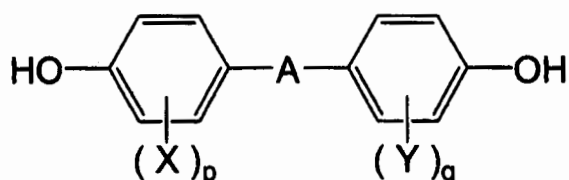
35 In the present invention, a polycarbonate resin is produced by melt polycondensation based on an ester exchange reaction between an aromatic dihydroxy compound and a carbonic diester.

Below described is a method for producing a polycarbonate resin by continuously conducting a melt polycondensation reaction using an aromatic dihydroxy compound and a carbonic diester as raw materials in the presence of an ester exchange catalyst.

40 (AROMATIC DIHYDROXY COMPOUND)

The aromatic dihydroxy compound used in the embodiment of the present invention may be a compound represented by the following formula (1).

Formula (1)



In the formula (1), A represents a single bond, a straight-chain, branched or cyclic divalent hydrocarbon group having from 1 to 10 carbon atoms which may be substituted, or a divalent group represented by -O-, -S-, -CO- or -SO₂-. X and Y each independently represent a halogen atom or a hydrocarbon group having from 1 to 6 carbon atoms. p and q each are independently an integer of from 0 to 2. X and Y, and p and q, each pair, may be the same or different.

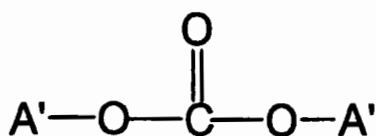
Specific examples of the aromatic dihydroxy compound include bisphenols such as bis(4-hydroxydiphenyl)methane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 2,2-bis(4-hydroxy-3-t-butylphenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 4,4-bis(4-hydroxyphenyl)heptane and 1,1-bis(4-hydroxyphenyl)cyclohexane; biphenols such as 4,4'-dihydroxybiphenyl and 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl; bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)ketone, and so on.

Of those, 2,2-bis(4-hydroxyphenyl)propane ("bisphenol A", which may be abbreviated hereinafter as BPA) is preferable. Those aromatic dihydroxy compounds can be used alone or as a mixture of two or more thereof.

(CARBONIC DIESTER)

The carbonic diester used in the embodiment of the present invention may be a compound represented by the following general formula (2).

Formula (2)



In the formula (2), A' represents a straight-chain, branched or cyclic monovalent hydrocarbon group having from 1 to 10 carbon atoms which may be substituted. Two A's may be the same or different.

Furthermore, examples of a substituent in the A' include an halogen atom, an alkyl group having from 1 to 10 carbon atoms, an alkoxy group having from 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.

Specific examples of the carbonic diester include diphenyl carbonate, a substituted diphenyl carbonate such as ditolyl carbonate; a dialkyl carbonate such as dimethyl carbonate, diethyl carbonate and di-t-butyl carbonate.

Of those, diphenyl carbonate (which may be abbreviated hereinafter as DPC) and a substituted diphenyl carbonate are preferable. Those carbonic diesters can be used alone or as a mixture of two or more thereof.

Furthermore, the carbonic diester may be replaced by a dicarboxylic acid or a dicarboxylic ester in an amount of preferably at most 50 mol%, further preferably at most 30 mol%.

The representative examples of the dicarboxylic acid or dicarboxylic ester include terephthalic acid, isophthalic acid, diphenyl terephthalate and diphenyl isophthalate. When the carbonic diester

is replaced by a dicarboxylic acid or a dicarboxylic ester, a polyester carbonate is obtained.

Those carbonic diesters (including the above substitutional dicarboxylic acid or dicarboxylic ester; the same also applies to the below) are used in an excess amount relative to the dihydroxy compound.

Namely, the carbonic diester is used in a molar ratio of preferably at least 1.01, particularly preferably at least 1.02, and preferably at most 1.30, particularly preferably at most 1.20, to the aromatic dihydroxy compound. When the molar ratio is less than 1.01, the amount of terminal OH group of a polycarbonate resin obtained increases and the thermal stability of the resin tends to deteriorate. On the other hand, when the molar ratio is more than 1.30, a reaction rate of the ester exchange decreases and there is the tendency that it is difficult to produce an aromatic polycarbonate resin having a desired molecular weight; in addition, an amount of the carbonic diester remaining in the resin becomes so large as to produce an unpleasant odor during the molding process or from a molding product, which is undesirable.

(ESTER EXCHANGE CATALYST)

The ester exchange catalyst used in the embodiment of the present invention may be one of catalysts generally used in producing an aromatic polycarbonate by an ester exchange method, and there are no particular restrictions thereon. In general, examples of the catalyst include basic compounds such as an alkali metal compound, a beryllium or magnesium compound, an alkaline earth metal compound, a basic boron compound, a basic phosphorus compound, a basic ammonium compound, and an amine compound.

Of those ester exchange catalysts, an alkali metal compound or an alkaline earth metal compound has a large effect in that a small amount of the thermal stabilizer is uniformly dispersed in the aromatic polycarbonate resin composition, which is the object of the embodiment of the present invention. Those ester exchange catalysts may be used alone or as a mixture of two or more thereof.

The ester exchange catalyst is generally used in a range of preferably at least 1×10^{-9} mol, particularly preferably at least 1×10^{-7} mol, and preferably at most 1×10^{-1} mol, particularly preferably at most 1×10^{-2} mol, per mole of the aromatic dihydroxy compound.

Examples of the alkali metal compound include inorganic alkali metal compounds such as hydroxides, carbonates and hydrogen carbonate compounds of alkali metals; and organic alkali metal compounds such as salts of alkali metals with alcohols, phenols or organic carboxylic acids. Examples of the alkali metals applicable herein include lithium, sodium, potassium, rubidium and cesium.

Of those alkali metal compounds, a cesium compound is preferable, and cesium carbonate, cesium hydrogen carbonate and cesium hydroxide are particularly preferable.

Examples of the beryllium or magnesium compound and the alkaline earth metal compound include inorganic alkaline earth metal compounds such as hydroxides or carbonates of beryllium, magnesium and alkaline earth metals; and salts of those metals with alcohols, phenols or organic carboxylic acids. Examples of the alkaline earth metals applicable herein include calcium, strontium and barium.

Examples of the basic boron compound include a sodium salt, a potassium salt, a lithium salt, a calcium salt, a magnesium salt, a barium salt and a strontium salt of a boron compound. Examples of the boron compound applicable herein include tetramethyl boron, tetraethyl boron, tetrapropyl boron, tetrabutyl boron, trimethylethyl boron, trimethylbenzyl boron, trimethylphenyl boron, triethylmethyl boron, triethylbenzyl boron, triethylphenyl boron, tributylbenzyl boron, tributylphenyl boron, tetraphenyl boron, benzyltriphenyl boron, methyltriphenyl boron and butyltriphenyl boron.

Examples of the basic phosphorus compound include trivalent phosphorus compounds such

as triethylphosphine, tri-n-propylphosphine, triisopropylphosphine, tri-n-butylphosphine, triphenylphosphine and tributylphosphine; and quaternary phosphonium salts derived from those compounds.

Examples of the basic ammonium compound include tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, trimethylethylammonium hydroxide, trimethylbenzylammonium hydroxide, trimethylphenylammonium hydroxide, triethylmethylammonium hydroxide, triethylbenzylammonium hydroxide, triethylphenylammonium hydroxide, tributylbenzylammonium hydroxide, tributylphenylammonium hydroxide, tetraphenylammonium hydroxide, benzyltriphenylammonium hydroxide, methyltriphenylammonium hydroxide and butyltriphenylammonium hydroxide.

Examples of the amine compound include 4-aminopyridine, 2-aminopyridine, N,N-dimethyl-4-aminopyridine, 4-diethylaminopyridine, 2-hydroxypyridine, 2-methoxypyridine, 4-methoxypyridine, 2-dimethylaminoimidazole, 2-methoxyimidazole, imidazole, 2-mercaptoimidazole, 2-methylimidazole and aminoquinoline.

(PRODUCTION METHOD OF AROMATIC POLYCARBONATE)

A production method of an aromatic polycarbonate will be described below.

The production of the aromatic polycarbonate is conducted by preparing a mixture containing an aromatic dihydroxy compound and a carbonic diester compound as raw materials (raw material preparation step) and subjecting the mixture of those compounds to a multi-stage polycondensation reaction in a molten state in the presence of an ester exchange reaction catalyst using plural reactors (polycondensation step). The reaction method may be any of a batchwise method, a continuous method, and a combination of a batchwise method and a continuous method, but the continuous method is preferable in view of the productivity and quality stability. In the case of the continuous method, reactors used generally comprise a plurality of reactors connected in series, preferably a plurality of vertical reactors and at least one horizontal reactor successive thereto.

The embodiment of the present invention employs, after the polycondensation step, an extruder for addition of a thermal stabilizer, preferably, a twin-screw extruder with a vent opening capable of volatilizing and removing unreacted raw materials and reaction by-products in a reaction melt.

Each of the steps in the production method will be described below.

(RAW MATERIAL PREPARATION STEP)

The aromatic dihydroxy compound and the carbonic diester used as raw materials of the aromatic polycarbonate are generally prepared as a molten mixture using a batchwise, semibatchwise or continuous stirring tank type apparatus in an atmosphere of an inert gas such as nitrogen or argon. In the case of using bisphenol A as the aromatic dihydroxy compound and diphenyl carbonate as the carbonic diester, for example, a temperature of the molten mixture is selected from a range of preferably at least 120°C, particularly preferably at least 125°C, and preferably at most 180°C, particularly preferably at most 160°C.

In this case, a mixing proportion of the aromatic dihydroxy compound and the carbonic diester is so adjusted that the carbonic diester is excess, and the carbonic diester is in a proportion of preferably at least 1.01, particularly preferably at least 1.02 mol, and preferably at most 1.30 mol, particularly preferably at most 1.20 mol, per mole of the aromatic dihydroxy compound.

(POLYCONDENSATION STEP)

Polycondensation by an ester exchange reaction between the aromatic dihydroxy compound and the carbonic diester is continuously conducted by a multi-stage method of generally at least 2 stages, and preferably from 3 to 7 stages.

Specific reaction conditions are as follows: a temperature is in a range of from 150°C to 320°C, a pressure is in a range of from ordinary pressure to 0.01 Torr (1.3 Pa), and an average

residence time per stage is in a range of from 5 minutes to 150 minutes.

When the polycondensation step is conducted by the multi-stage method, the temperature and vacuum are generally set to become higher stepwise within the above reaction conditions in each of reactors, in order to effectively discharge phenol produced as a by-product with the progress of the polycondensation reaction. Here, it is preferable to set the temperature as low as possible and the residence time as short as possible, to prevent deterioration of quality such as a hue of the aromatic polycarbonate resin obtained.

When the polycondensation step is conducted by the multi-stage method, it is preferable to provide a plurality of vertical reactors and/or at least one reactor with excellent thin-film evaporation performance successive thereto, thereby increasing an average molecular weight of the aromatic polycarbonate resin. The number of the reactors provided is generally 3 to 6, and preferably 4 or 5.

Here, the reactors with excellent thin-film evaporation performance used may be, for example, thin-film reactors, centrifugal thin-film evaporation reactors, surface renewal type twin screw kneading reactors, twin screw horizontal stirring reactors, wet wall type reactors, porous plate type reactors in which polymerization proceeds during a free fall, and porous plate type reactors in which polymerization proceeds during a fall along a wire.

Examples of the type of the stirring blade in the vertical reactor include a turbine blade, a paddle blade, a fardler blade, an anchor blade, a FULLZONE blade (manufactured by Kobelco Eco-Solutions Co., Ltd.), a SANMELER blade (manufactured by Mitsubishi Heavy Industries, Ltd.), a MAXBLEND blade (manufactured by SHI Mechanical & Equipment Inc.), a helical ribbon blade, and a lattice type twisting blade (manufactured by Hitachi Plant Technologies, Ltd.).

Furthermore, the horizontal reactor refers to a reactor with a stirring blade a revolution axis of which is horizontal (horizontal direction). Examples of the stirring blade in the horizontal reactor include single shaft stirring blades such as a disc type and a paddle type, and two shaft stirring blades such as HVR, SCR and N-SCR (manufactured by Mitsubishi Heavy Industries, Ltd.), Bivolac (manufactured by SHI Mechanical & Equipment Inc.), and a spectacle-shaped blade and a lattice type blade (manufactured by Hitachi Plant Technologies, Ltd.).

Moreover, the ester exchange catalyst used in the polycondensation of the aromatic dihydroxy compound and the carbonic diester compound is generally previously prepared as an aqueous solution. There are no particular restrictions on a concentration of the aqueous solution of the catalyst, and it is adjusted to an optional concentration according to a solubility of the catalyst in water. Another organic solvent such as acetone, alcohol, toluene or phenol can also be used in place of water.

There are no particular restrictions on the water used for dissolution of the catalyst as long as kinds and concentrations of impurities contained therein are constant. In general, distilled water, deionized water or the like is preferably used.

(PRODUCTION APPARATUS)

An example of the production method of the aromatic polycarbonate resin composition to which the embodiment of the present invention is applied will be specifically described below based on the drawings.

Fig. 1 is a drawing to show an example of a production apparatus of the aromatic polycarbonate resin composition. In the production apparatus shown in Fig. 1, the aromatic polycarbonate is produced through the raw material preparation step to prepare the raw materials of the aromatic dihydroxy compound and the carbonic diester, and the polycondensation step to perform the polycondensation reaction of those raw materials in a molten state using plural reactors.

Thereafter, pellets of the aromatic polycarbonate resin composition are formed through a step of terminating the reaction, and volatilizing and removing unreacted raw materials and reaction by-products in the polymerization reaction solution, a step of adding a thermal stabilizer, a releasing

agent, a coloring material, or the like, and a step of forming pellets of the aromatic polycarbonate resin in a predetermined particle size.

In the raw material preparation step, there are provided a first raw material preparation tank 2a and a second raw material preparation tank 2b connected in series, and a raw material supply pump 4a for supplying the raw materials prepared, to the polycondensation step. For example, anchor type stirring blades 3a and 3b are provided in the first raw material preparation tank 2a and the second raw material preparation tank 2b, respectively.

Furthermore, supplied to the first raw material preparation tank 2a are DPC in a molten state through a DPC supply port 1a-1, and bisphenol A (which may be referred to hereinafter as BPA) as an aromatic dihydroxy compound in a powder state through a BPA supply port 1b, whereby bisphenol A is dissolved in the molten diphenyl carbonate.

Next, in the polycondensation step, there are provided a first vertical reactor 6a, a second vertical reactor 6b and a third vertical reactor 6c which are connected in series, and a fourth horizontal reactor 9a serially connected as the subsequent stage to the third vertical reactor 6c. MAXBLEND blades 7a, 7b and 7c are provided in the first vertical reactor 6a, the second vertical reactor 6b and the third vertical reactor 6c, respectively. Furthermore, a lattice type blade 10a is provided in the fourth horizontal reactor 9a.

Furthermore, distillation pipes 8a, 8b, 8c and 8d for discharging by-products or the like produced by the polycondensation reaction are attached to the respective four reactors. The distillation pipes 8a, 8b, 8c and 8d are connected to condensers 81a, 81b, 81c and 81d, respectively, and the reactors are maintained in a predetermined reduced pressure state by respective depressurizers 82a, 82b, 82c and 82d.

In the production apparatus of the aromatic polycarbonate resin composition shown in Fig. 1, the DPC melt prepared at a predetermined temperature in a nitrogen gas atmosphere and the BPA powder weighed in a nitrogen gas atmosphere are continuously supplied to the first raw material preparation tank 2a through the DPC supply port 1a-1 and through the BPA supply port 1b, respectively. When a liquid level of the first raw material preparation tank 2a exceeds the same level as the maximum level in a transfer pipe, the mixture of raw materials is transferred to the second raw material preparation tank 2b.

Next, the mixture of raw materials is continuously supplied to the first vertical reactor 6a through the raw material supply pump 4a. Furthermore, an aqueous solution of cesium carbonate as a catalyst is continuously supplied through a catalyst supply port 5a at a halfway position of the transport pipe for the mixture of raw materials.

In the first vertical reactor 6a, the polycondensation reaction is conducted in a nitrogen atmosphere, for example, under the conditions of a temperature of 220°C, a pressure of 13.33 kPa (100 Torr) and the number of revolutions of MAXBLEND blade 7a of 160 rpm, while distilling by-product phenol off through the distillation pipe 8a and maintaining the liquid level constant so that an average residence time is 60 minutes. Next, the polymerization reaction solution discharged from the first vertical reactor 6a is then continuously supplied to the second vertical reactor 6b, the third vertical reactor 6c and the fourth horizontal reactor 9a successively so that the polycondensation reaction proceeds. The reaction conditions in the respective reactors are normally set to be increase the temperature, increase the degree of vacuum and decrease the stirring rate with the progress of the polycondensation reaction, and they are appropriately adjusted based on required performance such as a desired molecular weight. During the polycondensation reaction, the liquid level is controlled such that the average residence time in each reactor is, for example, about 60 minutes, and furthermore, in each reactor, by-product phenol is distilled off through the distillation pipe 8b, 8c or 8d.

Furthermore, in the embodiment of the present invention, by-products such as phenol are

continuously liquefied and recovered from the condensers 81a and 81b attached to the first vertical reactor 6a and the second vertical reactor 6b, respectively. Moreover, cold traps (not shown) are provided between the condensers 81c, 81d, and the depressurizers 82c, 82d attached to the third vertical reactor 6c and to the fourth horizontal reactor 9a, respectively, to continuously liquefy or solidify to recover by-products.

Next, the aromatic polycarbonate discharged from the fourth horizontal reactor 9a is supplied as kept in the molten state to a twin-screw extruder 11a having three vent port. Various types of additives such as a thermal stabilizer, an antioxidant, a weather resistant agent, a releasing agent, a lubricant, an antistatic agent, a plasticizer, a pigment, a dyestuff, a filler, a reinforcing agent, a flame retardant, and a polymer, e.g., another resin or rubber are supplied each into the extruder 11a through additive supply lines 12a, 12b, and 12c.

Here, the thermal stabilizer may be a phosphorus type stabilizer, a hindered phenol type stabilizer, a sulfur type stabilizer, an epoxy type stabilizer, a hindered amine type stabilizer, or the like. Specific examples of the thermal stabilizer preferably applicable will be described below.

These thermal stabilizers may be used singly or in combination of two or more compounds. There are no particular restrictions on an amount to be added and it is normally used in a range of from 0.0001 part to 0.5 part by weight, and preferably in a range of from 0.001 part to 0.2 part by weight, to 100 parts by weight of the aromatic polycarbonate. Among others, in a case where the thermal stabilizer is supplied in a liquid state, the amount is at most 0.005 part by weight, preferably at most 0.002 part by weight, more preferably at most 0.001 part by weight.

In the embodiment of the present invention here, the thermal stabilizer is continuously attached to aromatic polycarbonate pellets and continuously supplied into the extruder 11a through the additive supply line 12a, as described below.

The aromatic polycarbonate and thermal stabilizer are melted and mixed inside the extruder 11a and extruded from an outlet port. The aromatic polycarbonate is formed in the form of strands by means of holes (not shown) provided in the outlet port when it is extruded from the extruder 11a.

Then the aromatic polycarbonate in the strand form is cooled with cooling water through a strand bath 13a, pelletized by a strand cutter 14a, subjected to removal of moisture by a sieve 15a and then introduced into product silos 16a, 16b.

Furthermore, in the preferred embodiment of the present invention, some of the aromatic polycarbonate resin composition (aromatic polycarbonate pellets) which is the final product or commercial product, is also introduced into a product silo 16c through a branched pipe branched off from the pneumatic transport pipe.

A compressed inert gas such as air or nitrogen is supplied to the pneumatic transport pipe from a compressor not shown in the drawing, whereby the aromatic polycarbonate pellets can be pneumatically transported.

(CONTINUOUS ATTACHMENT OF THERMAL STABILIZER)

In the embodiment of the present invention, the aromatic polycarbonate pellets stored in the product silo 16c are, preferably continuously, supplied through the pneumatic transport pipe to a blender 21a, as occasion demands. In order to stably conduct the continuous supply to the blender 21a, though not shown in Fig. 1, it is also possible to adopt a configuration wherein a hopper and a volumetric feeder are provided for supplying the aromatic polycarbonate pellets, supply from the product silo 16c to the hopper is intermittently conducted, and the aromatic polycarbonate pellets are continuously supplied from the hopper to the blender 21a by the quantitative feeder.

The thermal stabilizer is continuously supplied to the blender 21a through a thermal stabilizer supply port 22a. Then the thermal stabilizer is continuously attached to the aromatic polycarbonate pellets in the blender 21a. A blending time is preferably in a range of from 1 minute to 20 minutes, more preferably in a range of from 5 minutes to 10 minutes. If the blending time is too long, the

apparatus tends to be too large; if it is too short, attachment to the whole of the aromatic polycarbonate pellets tends to be insufficient.

In this case, there are no particular restrictions on an amount of the thermal stabilizer continuously attached to the aromatic polycarbonate pellets in the blender 21a, but it is usually in a range of from 0.001 part to 1 part by weight, preferably from 0.005 part to 0.5 part by weight, more preferably from 0.01 part to 0.2 part by weight to 100 parts by weight of the aromatic polycarbonate pellets.

If the amount of the thermal stabilizer attached to the aromatic polycarbonate pellets is excessive, it results in degradation of dispersibility of the thermal stabilizer in the extruder 11a, and thus tends to cause deterioration of a color tone, and nonuniform quality of the aromatic polycarbonate obtained as a commercial product. Furthermore, if the amount of the thermal stabilizer attached to the aromatic polycarbonate pellets is too small, an amount of the pellets supplied into the extruder 11a tends to increase in order to keep a predetermined amount of the thermal stabilizer. This case results in supplying a large amount of the aromatic polycarbonate pellets preliminarily subjected to a thermal history, into the extruder 11a. As a result, there occurs not only the deterioration of the color tone of the aromatic polycarbonate obtained as a commercial product, but also an unstable operation of the extruder 11a, and an excessive load tends to be exerted on the blender 21a.

(CONTINUOUS ADDITION OF AROMATIC POLYCARBONATE PELLETS)

Next, the aromatic polycarbonate pellets to which the thermal stabilizer has been continuously attached in the blender 21a are continuously recycled through the additive supply line 12a into the extruder 11a and mixed with the aromatic polycarbonate in the molten state in the extruder 11a, as described above.

It is noted that the attachment here means such a state that the thermal stabilizer is adhered on the aromatic polycarbonate pellets by mixing.

There are no particular restrictions on the blender 21a as long as it is capable of continuously mixing, and it may be, for example, a ribbon blender or the like. Furthermore, because the aromatic polycarbonate pellets deteriorate in the product quality due to accompanying oxygen during supply into the extruder 11a, it is preferable to handle them in an inert gas atmosphere such as nitrogen. In particular, it is effective to introduce nitrogen into the blender 21a, for suppressing the thermal deterioration of the commercial product.

Furthermore, plural types of thermal stabilizers may be supplied into the blender 21a and other additives, e.g., a releasing agent, a coloring material and an ultraviolet absorber may be simultaneously supplied in addition to the thermal stabilizer.

Moreover, the additives supplied through the additive supply lines 12b and 12c may be supplied in the same manner as those through the additive supply line 12a.

An amount of the aromatic polycarbonate resin composition continuously recycled into the extruder 11a is normally in a range of from 0.1 part to 10 parts by weight, preferably from 0.5 part to 5 parts by weight, more preferably from 1 part to 4 parts by weight, based on 100 parts by weight of the aromatic polycarbonate supplied from the fourth horizontal reactor 9a into the extruder 11a. If the amount of the aromatic polycarbonate resin composition recycled to the extruder 11a is too small, the effect of the present invention is unlikely to be achieved; if it is too large, the thermal stability of the product is likely to deteriorate.

There are no particular restrictions on a size, shape and others of the aromatic polycarbonate pellets, and normally the size is preferably one resulting from processing to the maximum length of at most 20 mm. The shape can be a granular form, an amorphous form, a flat plate form, a cylindrical form, or the like; among others, the granular form and cylindrical form are preferable and the cylindrical form is particularly preferable because of easy availability.

In the embodiment of the present invention, some of the aromatic polycarbonate pellets pelletized as the commercial product are taken out, the thermal stabilizer is continuously attached thereto and the thermal stabilizer attached to pellets is further continuously supplied to the extruder, as described above. Therefore, it becomes feasible to uniformly mix the thermal stabilizer in the aromatic polycarbonate resin in the molten state in the extruder. Furthermore, the pellets to which the thermal stabilizer has been continuously attached are continuously supplied into the extruder, so that the aromatic polycarbonate resin composition with stable quality can be obtained without alteration or separation of the thermal stabilizer.

Moreover, in the embodiment of the present invention, the aromatic polycarbonate pellets supplied from the product silo 16c themselves contain the thermal stabilizer, the thermal stabilizer is further attached to the pellets, and then the pellets are supplied into the extruder 11a. Therefore, the thermal stability of the aromatic polycarbonate resin thus obtained is dramatically improved and degradation of the quality of the final product can be remarkably decreased.

Since the embodiment of the present invention adopts the above-described technique, the thermal stabilizer can be sufficiently dispersed in the aromatic polycarbonate resin composition even though the amount of the thermal stabilizer is small. Particularly, in the embodiment of the present invention, even in the case where the amount of the thermal stabilizer is at most 0.002 part by weight relative to 100 parts by weight of the aromatic polycarbonate resin in the molten state in the extruder 11a, the thermal stabilizer can be stably supplied to the aromatic polycarbonate resin.

The embodiment of the present invention is particularly effective in cases where the thermal stabilizer used is liquid and is an acidic compound or its derivative.

Here, there are no particular restrictions on the acidic compound used as the thermal stabilizer, and for example, it may be normally a compound to neutralize the basic ester exchange catalyst used in the polycondensation reaction (compound so-called a reaction terminator or a deactivating compound).

Specific examples of the compound include Bronsted acids such as hydrochloric acid, nitric acid, boric acid, sulfuric acid, sulfurous acid, phosphoric acid, phosphorous acid, hypophosphorous acid, polyphosphoric acid, adipic acid, ascorbic acid, asparatic acid, azelaic acid, adenosine phosphate, benzoic acid, formic acid, valeric acid, citric acid, glycolic acid, glutamic acid, glutaric acid, cinnamic acid, succinic acid, acetic acid, tartaric acid, oxalic acid, p-toluenesulfinic acid, p-toluenesulfonic acid, naphthalenesulfonic acid, nicotinic acid, picric acid, picolinic acid, phthalic acid, terephthalic acid, propionic acid, benzenesulfinic acid, benzenesulfonic acid, malonic acid and maleic acid; and esters, acid halides and salts thereof, and so on. They may be used singly or in combination of two or more compounds.

Of those acidic compounds, preferred acidic compounds are a sulfonic acid which is liquid and which may be substituted with a C_{1-10} alkyl group, or its esters. Examples of the sulfonic acid include benzenesulfonic acid, toluenesulfonic acid, naphthalenesulfonic acid and so on. Examples of the ester of the sulfonic acid include a methyl ester, ethyl ester, butyl ester, octyl ester, phenyl ester and so on of the sulfonic acid. Of those, butyl p-toluenesulfonate is particularly preferable.

In the embodiment of the present invention, a viscosity average molecular weight (Mv_1) of the aromatic polycarbonate in the aromatic polycarbonate pellets to which the thermal stabilizer is attached is preferably at most a viscosity average molecular weight (Mv_2) of the aromatic polycarbonate in the molten state in the extruder 11a. Namely, a preferred condition is $Mv_1 \leq Mv_2$. Among them, the difference between the viscosity average molecular weights, ($Mv_2 - Mv_1$), is at most 5,000, preferably at most 3,000 and particularly preferably at most 2,000.

If the viscosity average molecular weight (Mv_1) of the aromatic polycarbonate in the aromatic polycarbonate pellets to which the thermal stabilizer is attached is excessively larger than the viscosity average molecular weight (Mv_2) of the aromatic polycarbonate in the molten state in the

extruder 11a, or if the difference ($Mv_2 - Mv_1$) between the viscosity average molecular weight (Mv_2) and the viscosity average molecular weight (Mv_1) is too large, the dispersibility of the thermal stabilizer tends to degrade.

Furthermore, because the embodiment of the present invention adopts the structure wherein the aromatic polycarbonate resin composition produced using the extruder 11a is used as the aromatic polycarbonate pellets to which the thermal stabilizer is attached, and wherein the pellets with the thermal stabilizer are recycled to the extruder 11a, it is possible to use a cutting-error product produced in the final stage of the method for producing the aromatic polycarbonate resin, a loss of production due to switching of products, and so on as the pellets to which the thermal stabilizer is attached. Furthermore, it is also effective for stabilizing the supply amount of the thermal stabilizer, ensuring the dispersibility of the thermal stabilizer in the molten polymer, preventing the thermal deterioration of the recycled product and thus maintaining the quality of product. As a result, we can expect simultaneous implementation of improvement in the yield of product, saving of resources, and stable quality of product.

Fig. 2 is a drawing to show another example of the production apparatus of the aromatic polycarbonate resin composition where additives such as the thermal stabilizer are attached using a plurality of blenders. The same structure as in Fig. 1 is denoted by the same reference symbols and explanation thereof is omitted herein.

In the production apparatus of the aromatic polycarbonate resin composition shown in Fig. 2, a blender 21b is further added to the production apparatus of the aromatic polycarbonate resin composition shown in Fig. 1. Furthermore, a thermal stabilizer supply port 22b is separately formed.

The aromatic polycarbonate pellets can be supplied to the blender 21b through a branched pipe branched off from the pneumatic transport pipe as in the case of the blender 21a. Furthermore, the thermal stabilizer and other additives can be supplied through the thermal stabilizer supply port 22b and they can be attached to the aromatic polycarbonate pellets in the blender 21b.

After the attachment of the thermal stabilizer and other additives in the blender 21b, the resulting pellets are recycled through the additive supply line 12b to the extruder 11a.

EXAMPLES

The specific embodiment of the present invention will be described below based on examples. However, the present invention is not limited to the following examples so far as it does not depart from its gist.

Furthermore, the polycarbonate resin compositions in the examples and comparative examples below were analyzed by the following methods.

(1) Viscosity Average Molecular Weight (Mv)

An aromatic polycarbonate resin composition was dissolved in methylene chloride; an intrinsic viscosity $[\eta]$ was measured at 20°C in methylene chloride with an Ubbelohde viscometer; and a viscosity average molecular weight (Mv) was obtained by the equation (1) below.

It should be noted that amounts of components other than the aromatic polycarbonate resin in the aromatic polycarbonate resin composition were so slight that the viscosity average molecular weight (Mv) of the aromatic polycarbonate resin in the aromatic polycarbonate resin composition was considered to be the same as the viscosity average molecular weight (Mv) of the aromatic polycarbonate resin composition.

$$[\eta] = 1.23 \times 10^{-4} (Mv)^{0.83} \quad \text{Equation (1)}$$

(2) Initial Hue

After an aromatic polycarbonate resin composition was dried at 120°C in a nitrogen atmosphere for 6 hours, the following molding operation was repeated: an injection molding piece having 60 mm×60 mm×3 mm thick was molded under the conditions of a resin temperature of 360°C

and a molding cycle of 30 seconds by a J75EII type injection molding machine manufactured by The Japan Steel Works, Ltd.

Then yellow index (YI) values of the injection molding products obtained in the sixth shot to fifteenth shot were measured with a color tester (CM-3700d manufactured by KONICA MINOLTA HOLDINGS, INC.) and an average value and standard deviation thereof were calculated. The smaller the YI value, the better the hue, which shows better quality; the smaller the standard deviation, the smaller the nonuniformity of hue, which shows stabler quality.

(3) Hue after Thermal Retention Test

The molding cycle was changed to 10 minutes for the sixteenth and subsequent shots in the above section (2) and the operation of injection molding was repeated to obtain injection molding products of the sixteenth to twenty second shots.

YI values of the injection molding products having 60 mm×60 mm×3 mm thick obtained in the twentieth shot to the twenty second shot were measured with a color tester (CM-3700d manufactured by KONICA MINOLTA HOLDINGS, INC.) and an average value was calculated. The smaller the value, the better the hue, which shows better quality.

EXAMPLE 1

The production apparatus as shown in Fig. 2 was used as the production apparatus of the aromatic polycarbonate resin composition.

In Fig. 2, DPC and BPA were continuously supplied at a constant molar ratio (DPC/BPA=1.050) in a nitrogen atmosphere through the DPC supply port 1a-1 and through the BPA supply port 1b, respectively, to the first raw material preparation tank 2a in which an internal temperature was controlled at 140°C, whereby they were brought into a uniform molten state.

Thereafter, the melt was continuously supplied through the second raw material preparation tank 2b also controlled at 140°C, to the first vertical reactor 6a by the raw material supply pump 4a so that a supply amount per unit time was constant. Then, an aqueous solution of cesium carbonate was continuously supplied as a catalyst through the catalyst supply port 5a so that its amount was 0.5×10^{-6} mole relative to 1 mole of BPA.

In the first vertical reactor 6a, the internal temperature and pressure were controlled at 220°C and 13.3 kPa, respectively, the opening of the valve (not shown) provided in the discharge line at the bottom part of the reactor was controlled so that an average retention time became 1.5 hours, and the level of the liquid surface was kept constant.

The polymerization liquid discharged from the first vertical reactor 6a was then continuously supplied to the second vertical reactor 6b, the third vertical reactor 6c and the fourth horizontal reactor 9a in succession. In the second vertical reactor 6b, the internal temperature, pressure and average retention time were 260°C, 4 kPa and 1.5 hours, respectively. Furthermore, in the third vertical reactor 6c, the internal temperature, pressure and average retention time were 270°C, 70 Pa and 1 hours, respectively, and in the fourth horizontal reactor 9a, the internal temperature, pressure and average retention time were 270°C, 200 Pa and 1.5 hours, respectively.

This aromatic polycarbonate was supplied as kept in the molten state to the twin-screw extruder 11a so that the supply amount per unit time became 97 parts by weight. On this occasion, the aromatic polycarbonate pellets containing the thermal stabilizer (average length: 3 mm, average diameter: 3 mm, $M_v=15,000$) which were produced in the same manner as described below, had been stocked in the product silo 16c and the pellets were supplied to the blender 21a so that a supply rate became 1.5 parts by weight per unit time. A continuous ribbon blender was used as the blender 21a and nitrogen was circulated therein. Furthermore, the blending time in the blender 21a was 8 minutes.

Moreover, butyl p-toluenesulfonate was supplied as a thermal stabilizer through the thermal stabilizer supply port 22a by a small-size volumetric pump (not shown) so that a supply rate per unit

time became 0.0005 part by weight, and continuously attached to the aromatic polycarbonate pellets. Then, the pellets were continuously supplied through the additive supply line 12a to the extruder 11a.

Furthermore, the aromatic polycarbonate pellets were supplied in the same manner as above to the blender 21b (a continuous ribbon blender used like the blender 21a) from the product silo 16c so that a supply rate per unit time became 1.5 parts by weight while nitrogen was circulated therein. Moreover, a blending time in the blender 21b was 8 minutes.

Here, tris(2,4-di-t-butylphenyl)phosphite was continuously supplied as a thermal stabilizer in an amount of 0.005 part by weight per unit time and stearic acid monoglyceride was continuously supplied as a releasing agent in an amount of 0.03 part by weight per unit time through the supply port 22b to the blender 21b. Then, they are continuously attached to the aromatic polycarbonate pellets and the pellets were continuously supplied through the additive supply line 12b to the extruder 11a.

The polycarbonate resin composition extruded in the strand form and in the molten state from the twin-screw extruder 11a was cooled and solidified in the strand bath 13a and pelletized by the strand cutter 14a, pellets of irregular size were removed by the sieve 15a, and the resultant pellets were appropriately stocked in the product silos 16a to 16c.

The viscosity average molecular weight (Mv) of the resultant polycarbonate resin composition was 15,000, the initial YI was 1.28, the standard deviation was 0.015 and YI after the retention thermal stability test was 3.21.

EXAMPLE 2

An aromatic polycarbonate resin composition was prepared in the same manner as in Example 1 except that the viscosity average molecular weight (Mv) of the aromatic polycarbonate pellets stocked in the product silo 16c was changed to 14,500.

The viscosity average molecular weight (Mv) of the resultant polycarbonate resin composition was 15,000, the initial YI was 1.25, the standard deviation was 0.013 and YI after the retention thermal stability test was 3.20.

EXAMPLE 3

An aromatic polycarbonate resin composition was prepared in the same manner as in Example 1 except that the viscosity average molecular weight (Mv) of the aromatic polycarbonate pellets stocked in the product silo 16c was 27,000.

The viscosity average molecular weight (Mv) of the resultant polycarbonate resin composition was 15,400, the initial YI was 1.37, the standard deviation was 0.031 and YI after the retention thermal stability test was 3.43.

EXAMPLE 4

An aromatic polycarbonate resin composition was produced in the same as in Example 1 except that the supply amounts of the aromatic polycarbonate pellets supplied to the blenders 21a and 21b were changed each to 3 parts by weight. The blending times each were 4 minutes.

The viscosity average molecular weight (Mv) of the resultant polycarbonate resin composition was 15,000, the initial YI was 1.40, the standard deviation was 0.012 and YI after the retention thermal stability test was 3.65.

COMPARATIVE EXAMPLE 1

An aromatic polycarbonate resin composition was prepared in the same manner as in Example 1 except that aromatic polycarbonate pellets containing no thermal stabilizer were stocked in the product silo 16c and supplied therefrom.

The viscosity average molecular weight (Mv) of the resultant polycarbonate resin composition was 15,000, the initial YI was 1.55, the standard deviation was 0.017, and YI after the retention thermal stability test was 3.90, which were worse than those in each of Examples above.

COMPARATIVE EXAMPLE 2

An aromatic polycarbonate resin composition was prepared in the same manner as in Comparative Example 1 except that no nitrogen was circulated in the blenders 21a and 21b.

The viscosity average molecular weight (Mv) of the resultant polycarbonate resin composition was 15,000, the initial YI was 1.59, the standard deviation was 0.024, and YI after the retention thermal stability test was 4.05, which were worse than those in each of Examples above.

COMPARATIVE EXAMPLE 3

6 parts by weight of the aromatic polycarbonate pellets having been stocked in the product silo 16c were charged in a Henschel mixer, 0.002 part by weight of butyl p-toluenesulfonate was added thereto, and they were sufficiently mixed for 10 minutes. The pellets prepared in the batch system as described above were supplied to the blender 21a so that a supply rate per unit time became 1.5 parts by weight. The continuous ribbon blender as in Example 1 was used as the blender 21a, and the operation was conducted in the same manner as in Example 1 except that butyl p-toluenesulfonate was not supplied through the thermal stabilizer supply port 22a.

The viscosity average molecular weight (Mv) of the resultant polycarbonate resin composition was 15,000, the initial YI was 1.49, the standard deviation was 0.157 and YI after the retention thermal stability test was 3.77.

COMPARATIVE EXAMPLE 4

In Comparative Example 3, 6 parts by weight of the aromatic polycarbonate pellets having been stocked in the product silo 16c, 0.02 part by weight of tris(2,4-di-t-butylphenyl)phosphite and 0.12 part by weight of stearic acid monoglyceride were preliminarily prepared in the batch system by sufficiently mixing them for 10 minutes with a Henschel mixer and the resultant pellets were continuously supplied to the blender 21b so that a supply rate per unit time became 1.5 parts by weight. The continuous ribbon blender as in Example 1 was used as the blender 21b, and the operation was conducted in the same manner as in Comparative Example 3 except that neither tris(2,4-di-t-butylphenyl)phosphite nor stearic acid monoglyceride was supplied through the supply port 22b. The viscosity average molecular weight (Mv) of the resultant polycarbonate resin composition was 15,000, the initial YI was 1.53, the standard deviation was 0.170 and YI after the retention thermal stability test was 3.84.

INDUSTRIAL APPLICABILITY

The present invention is industrially useful because it permits production of the aromatic polycarbonate resin composition with stable quality such as thermal stability, while improving the yield of product and contributing to saving of natural resources.

The entire disclosure of Japanese Patent Application No. 2007-120090 filed on April 27, 2007 including the specification, claims, drawings and summary is incorporated herein by reference in its entirety.

CLAIMS:

1. A method for producing an aromatic polycarbonate resin composition containing a thermal stabilizer, the method comprising the following steps:

a polycarbonate supply step of continuously supplying an aromatic polycarbonate in a molten state to an extruder;

an extrusion step of mixing the aromatic polycarbonate supplied from the polycarbonate supply step, with the thermal stabilizer in the extruder to obtain an aromatic polycarbonate mixture, and extruding the aromatic polycarbonate mixture from the extruder;

a pellet formation step of pelletizing the aromatic polycarbonate mixture extruded from the extruder in the extrusion step, to form aromatic polycarbonate pellets; and

a pellet recycle step of taking some of the aromatic polycarbonate pellets pelletized in the pellet formation step, continuously attaching the thermal stabilizer to the pellets, and continuously supplying the thermal stabilizer-attached pellets to the extruder into which the aromatic polycarbonate is supplied in the polycarbonate supply step.

2. The method for producing the aromatic polycarbonate resin composition according to Claim 1, further comprising a pneumatic transport step of pneumatically transporting the aromatic polycarbonate pellets pelletized in the pellet formation step, through a transport pipe,

wherein some of the aromatic polycarbonate pellets pelletized in the pellet formation step are pneumatically transported through a branched pipe branched off from the transport pipe.

3. The method for producing the aromatic polycarbonate resin composition according to Claim 1 or 2, wherein the thermal stabilizer attached to the aromatic polycarbonate pellets in the pellet recycle step is in a liquid state.

4. The method for producing the aromatic polycarbonate resin composition according to any one of Claims 1 to 3, wherein the thermal stabilizer attached to the aromatic polycarbonate pellets in the pellet recycle step is an acidic compound or a derivative thereof.

5. The method for producing the aromatic polycarbonate resin composition according to any one of Claims 1 to 4, wherein the thermal stabilizer is a sulfonic acid or its ester which is in a liquid state and which may be substituted with a C₁₋₁₀ alkyl group.

6. The method for producing the aromatic polycarbonate resin composition according to any one of Claims 1 to 5, wherein the pellet recycle step comprises continuously attaching the thermal stabilizer to the aromatic polycarbonate pellets, in an amount of from 0.001 part to 1 part by weight to 100 parts by weight of the aromatic polycarbonate pellets.

7. The method for producing the aromatic polycarbonate resin composition according to any one of Claims 1 to 6, wherein the pellet recycle step comprises supplying to the extruder the stabilizer-attached aromatic polycarbonate pellets in an amount of from 0.5 part to 5 parts by weight to 100 parts by weight of the aromatic polycarbonate to be supplied to the extruder.

8. The method for producing the aromatic polycarbonate resin composition according to any one of Claims 1 to 7, wherein a viscosity average molecular weight (Mv_1) of the aromatic polycarbonate pelletized in the pellet formation step is not more than a viscosity average molecular weight (Mv_2) of the aromatic polycarbonate in the molten state mixed with the thermal stabilizer in the extruder in the extrusion step ($Mv_1 \leq Mv_2$).

9. The method for producing the aromatic polycarbonate resin composition according to any one of Claims 1 to 8, wherein the extrusion step comprises mixing the thermal stabilizer in an amount of at most 0.002 part by weight to 100 parts by weight of the aromatic polycarbonate.

10. The method for producing the aromatic polycarbonate resin composition according to any one of Claims 1 to 9, wherein the polycarbonate supply step comprises obtaining the aromatic polycarbonate to be supplied to the extruder, by a polycondensation reaction of an aromatic dihydroxy compound and a carbonic diester in the presence of a basic compound as a catalyst.