

DESCRIPTION

DEVOLATILIZING EXTRUDER, AND DEVOLATILIZING EXTRUSION
METHOD OF POLYMER COMPOSITION USING THE SAME AND METHOD OF
5 PRODUCING POLYMER

Technical Field

[0001]

The present invention relates to a devolatilizing
extruder to be used in a production of a polymer, and a
10 method for devolatilizing extrusion of a polymer
composition using the same, and a method for producing a
polymer.

Background Art

[0002]

15 There have been known, as a method for producing a
polymer such as a (meth)acrylic polymer, methods in which a
polymer composition containing a polymer and a volatile
component is obtained by a solution polymerization method
or a bulk polymerization method, and then the obtained
20 polymer composition is supplied to a screw type
devolatilizing extruder to remove a volatile component,
thus obtaining a polymer (see, for example, Patent
Documents 1 and 2).

Prior Art Documents

25 Patent Documents

[0003]

Patent Document 1: JP-A-3-49925

Patent Document 2: JP-A-2003-96105

Disclosure of the Invention

5 Problems to be Solved by the Invention

[0004]

In a screw inserted into a devolatilizing extruder, a shaft portion is supported by a shaft seal bearing portion of the devolatilizing extruder and a shaft seal portion is provided around the shaft portion of the screw in the shaft seal bearing portion. A devolatilizing extrusion method using a conventional devolatilizing extruder had a problem that, when an operation is continuously carried out over a long period, an unreacted monomer or a polymer thereof in a polymer composition adheres to this shaft seal bearing portion and poor rotation of the screw arises, and thus it becomes difficult to operate the devolatilizing extruder.

[0005]

In light of the problem of the prior art, the present invention had been made and an object thereof is to provide a devolatilizing extruder that can prevent an unreacted monomer and a polymer thereof from adhering to the shaft seal bearing portion during operation, and a method for devolatilizing extrusion of a polymer composition using the same and a method for producing a polymer.

Means for Solving the Problems

[0006]

In order to achieve the aforementioned object, the present invention provides a devolatilizing extruder comprising: a cylinder having a polymer composition supply port, a gas discharge port, a polymer outlet and a through-hole; a rotatable screw inserted into the cylinder through the through-hole; and a shaft seal bearing portion supporting a shaft portion of the screw extending from the through-hole to the outside of the cylinder; wherein the shaft seal bearing portion includes a shaft seal portion, a cavity portion formed between the shaft seal portion and the cylinder, and a liquid introduction port for introducing a liquid containing a polymerization inhibitor into the cavity portion, and also the shaft seal bearing portion has a gap that serves as a flow path, through which a liquid introduced into the cavity portion through the liquid introduction port is discharged into the cylinder, between an inner wall face of the through-hole and a surface of the shaft portion of the screw.

[0007]

A conventional devolatilizing extruder had a problem that, when a polymer is continuously produced over a long period, an unreacted monomer, a polymer thereof and the like contained in a volatile component adhere in the

vicinity of a shaft seal bearing portion in a devolatilizing extruder, thus causing poor rotation of a screw. It is considered that the unreacted monomer contained in the volatile component adheres in the vicinity
5 of the shaft seal bearing portion and thus the monomer is converted into a polymer as a result of polymerization due to heat. In the devolatilizing extruder of the present invention, since a liquid introduction port for introducing a liquid into a cavity portion between a shaft seal portion
10 in the shaft seal bearing portion and a cylinder is provided, the introduced liquid passes through a gap between a through-hole and a shaft portion of a screw, and then the liquid is introduced into the cylinder. Therefore, flow of the liquid toward the cylinder from the shaft seal
15 bearing portion is formed, and thus it becomes difficult for the unreacted monomer to reach in the vicinity of the shaft seal bearing portion. In addition, since the liquid introduced into the cylinder contains a polymerization inhibitor, a polymerization reaction of the unreacted
20 monomer in the vicinity of shaft seal bearing portion is also suppressed. As a result, adhesion of the unreacted monomer and a polymer thereof in the vicinity of shaft seal bearing portion is sufficiently suppressed and it becomes possible to sufficiently suppress poor rotation of the
25 screw even though the operation is continuously carried out

over a long period.

[0008]

In the devolatilizing extruder of the present invention, the shaft seal portion is preferably formed of a mechanical seal. Thereby, degradation of the shaft seal
5 portion does not arise and thus continuous operation can be stably carried out even at a high temperature over a long period.

[0009]

10 The present invention also provides a method for devolatilizing extrusion of a polymer composition, comprising: supplying a polymer composition containing a polymer and a volatile component into the cylinder through the polymer composition supply port in the devolatilizing
15 extruder of the present invention and also supplying liquid to the cavity portion through the liquid introduction port to discharge the volatile component through the gas discharge port and to discharge a polymer after devolatilization through the polymer outlet, respectively.

20 [0010]

According to such a devolatilizing extrusion method, since the devolatilizing extruder of the present invention is used, it is possible to sufficiently suppress an unreacted monomer, a polymer thereof and the like contained
25 in a volatile component from adhering in the vicinity of a

shaft seal bearing portion of a devolatilizing extruder,
and to continuously carry out a devolatilizing extrusion
treatment of a polymer composition over a long period
without causing a problem such as poor rotation of a screw.

5 [0011]

The present invention also provides a method for
producing a polymer, comprising the steps of: continuously
supplying a raw material containing a monomer, a radical
polymerization initiator and a chain transfer agent into a
10 polymerization reaction vessel; polymerizing the monomer in
the polymerization reaction vessel to obtain a polymer
composition containing a polymer and a volatile component
containing the unreacted monomer; and supplying the polymer
composition into the cylinder through the polymer
15 composition supply port into the devolatilizing extruder of
the present invention and also supplying liquid to the
cavity portion through the liquid introduction port to
discharge the volatile component through the gas discharge
port and to discharge a polymer after devolatilization
20 through the polymer outlet, respectively.

[0012]

According to the method for producing a polymer,
since the devolatilizing extruder of the present invention
is used, it is possible to sufficiently suppress an
25 unreacted monomer, a polymer thereof and the like contained

in a volatile component from adhering in the vicinity of a shaft seal bearing portion of a devolatilizing extruder in the step of carrying out a devolatilizing extrusion treatment, and to continuously produce a polymer composition over a long period without causing a problem such as poor rotation of a screw.

[0013]

In the aforementioned method for devolatilizing extrusion of a polymer composition and method for producing a polymer of the present invention, the liquid supplied through the liquid introduction port is preferably a liquid prepared by dissolving the polymerization inhibitor in a monomer used as a raw material of the polymer. In such the liquid, the monomer, that is the same component as that of an unreacted monomer contained in a polymer composition, is used as a solvent that dissolves a polymerization inhibitor. Therefore, when compared with the case of using the other solvent, it is possible to suppress impurities from mixing in the obtained polymer.

Effects of the Invention

[0014]

According to the present invention, it is possible to provide a devolatilizing extruder that can suppress an unreacted monomer and a polymer thereof from adhering to a shaft seal bearing portion during operation, and also can

continuously operate over a long period without causing poor rotation of the screw; and a method for devolatilizing extrusion of a polymer composition using the same, and a method for producing the polymer.

5 Brief Description of the Drawings

[0015]

Fig. 1 is a schematic view showing an internal structure of a devolatilizing extruder according to preferred embodiment of the present invention.

10 Fig. 2 is a partial sectional view of a shaft seal bearing portion of a devolatilizing extruder according to preferred embodiment of the present invention.

Fig. 3 is a schematic block diagram showing a production system of a polymer using a devolatilizing
15 extruder of the present invention.

Mode for Carrying Out the Invention

[0016]

Preferred embodiments of the present invention will be described in detail with reference to the accompanying
20 drawings. The same numerals are used for the same or identical portions in the drawings, and repetitive descriptions are omitted. Also, dimensional ratios of the drawings are not limited to the illustrated ratios

[0017]

25 Fig. 1 is a schematic view showing an internal

structure of a devolatilizing extruder according to preferred embodiment of the present invention. As shown in Fig. 1, a devolatilizing extruder 100 includes a cylinder 10 that includes a polymer composition supply port 12 for supplying a polymer composition containing a polymer and a volatile component, a gas discharge port 14 for discharging a volatile component, a polymer outlet 16 for discharging a polymer after devolatilization, and a through-hole 18; a rotatable screw 20 inserted into the cylinder 10 through the through-hole 18; and a shaft seal bearing portion 30 that supports a shaft portion 20a of the screw 20 extending from the through-hole 18 to the outside of the cylinder 10. The cylinder 10 is provided with four gas discharge ports 14, and one gas discharge port (back vent) 14a is provided at the side of the shaft seal bearing portion 30 when viewed from the polymer composition supply port 12, and three gas discharge ports (fore vents) 14b, 14c, 14d are respectively provided at the side of the polymer outlet 16. The shaft seal bearing portion 30 includes a shaft seal portion 32, a cavity portion 34 formed between the shaft seal portion and the cylinder 10, and a liquid introduction port 36 for introducing a liquid containing a polymerization inhibitor into the cavity portion 34.

[0018]

Fig. 2 is a partial sectional view of a shaft seal

bearing portion of a devolatilizing extruder according to preferred embodiment of the present invention. In the present embodiment, the shaft seal portion 32 is formed of a mechanical seal. Between the shaft seal portion 32 and the cylinder 10, the cavity portion 34 is formed. The interior of the shaft seal bearing portion 30 and the interior of the cylinder 10 are connected through a through-hole 18 and a shaft portion 20a of the screw 20 passes through this through-hole 18. A driving device (not shown) for rotationally driving the screw 20 is provided on the opposite side of the cylinder 10 of the shaft seal portion 32. As shown in Fig. 2, in a boundary portion between the shaft seal bearing portion 30 and the cylinder 10, a gap exists between an inner wall face of the through-hole 18 and a surface of the shaft portion 20a of the screw 20, and the liquid containing a polymerization inhibitor introduced into the cavity portion 34 from the liquid introduction port 36 is discharged into the cylinder through this gap as a flow path FP. The liquid discharged into the cylinder 10 is discharged out of the cylinder 10 through the gas discharge port 14, together with the volatile component in the polymer composition. A part of the polymerization inhibitor in the liquid is discharged through the gas discharge port 14, and also remains in the polymer and is discharged through a polymer outlet 16,

together with the polymer.

[0019]

The shaft seal portion 32 may be formed in a form of a known shaft seal and is preferably formed of a mechanical seal since a problem such as seal failure is less likely to arise due to an influence of the liquid introduced into the cavity portion 34. There is no particular limitation on the type of the mechanical seal, and a known type mechanical seal can be used. For example, as shown in Fig. 2, the mechanical seal includes a rotating ring 32a fixed on the side of a screw 20 and a fixed ring 32b fixed on the side of a shaft seal bearing portion body (casing), and is constituted so that the rotating ring 32a and the fixed ring 32b are pressed by a given force using a spring (not shown) or the like and thus they tightly adhere to each other. In order to decrease friction of a contact surface between the rotating ring 32a and the fixed ring 32b, a mechanical seal liquid 32c is filled into the mechanical seal 32. In Fig. 2, a constitution of a mechanical seal including two pair of combinations of the rotating ring 32a and the fixed ring 32b, namely, a double mechanical seal is shown. Usually, the mechanical seal liquid 32c is continuously supplied through a mechanical seal liquid introduction port (not shown) using a pump or the like, and then continuously discharged through a mechanical seal

liquid discharge port (not shown). It is preferred that the mechanical seal liquid is circulatorily supplied. The filling pressure is appropriately set according to the size, extrusion conditions and the like of the devolatilizing extruder, and is set to a pressure higher than that of the liquid to be introduced into the cavity portion 34.

[0020]

It is possible to use, as the mechanical seal liquid 32c, a known mechanical seal liquid without any limitation. Specific examples thereof include an adipate ester, a phthalate ester, a diisobutyrate ester, acetylated glyceride and the like. Examples of the adipate ester include bis(2-ethylhexyl) adipate, diisononyl adipate, diisodecyl adipate and the like. Examples of the phthalate ester include bis(2-ethylhexyl) phthalate, diisononyl phthalate, diisodecyl phthalate and the like. Examples of the diisobutyrate ester include 2,2,4-trimethyl-1,3-pentanediol diisobutyrate and the like. Examples of the acetylated glyceride include glycerin diacetomonolaurate, glycerin diacetomonostearate, glycerin diacetomonooleate, glycerin diacetomonolinoleate, glycerin diacetomono 12-hydroxystearate, glycerin diacetomonomyristate, glycerin diacetomonopalmitate, glycerin monoacetomonostearate, glycerin monoacetomonomyristate, glycerin monoacetomonopalmitate, glycerin monoacetomonoricinoleate,

glycerin monoacetomono 12-hydroxystearate, glycerin
monoacetomonobehenate, glycerin monoacetomonooleate,
glycerin monoacetomonolaurate, glycerin monoacetodioleate,
glycerin monoacetodiricinoleate, glycerin
5 monoacetodicaprylate, glycerin monoacetodilaurate, glycerin
monoacetodistearate and the like. Among these, an adipate
ester and a diisobutyrate ester are preferred, and an
adipate ester is particularly preferred. The adipate ester
has a merit that, when a (meth)acrylic polymer,
10 particularly polymethyl methacrylate (PMMA) is produced as
a polymer, the adipate ester does not accelerate a
polymerization reaction of an unreacted monomer even if
mixed in a polymer composition, and is also less likely to
cause an adverse influence such as coloration of the
15 obtained polymer.

[0021]

The shaft seal portion 32 can also be formed of, in
addition to a mechanical seal, a gland packing, a Wilson
seal, an oil seal, a labyrinth seal, an o-ring seal, a
20 bellows seal and the like.

[0022]

The liquid to be introduced into the cavity portion
34 through the liquid introduction port 36 is preferably a
liquid containing a polymerization inhibitor, which is
25 prepared by dissolving a polymerization inhibitor in a

solvent that does not accelerate a polymerization reaction of an unreacted monomer. Examples of the solvent include organic solvents such as toluene, xylene, ethylbenzene, methyl isobutyl ketone, methyl alcohol, ethyl alcohol, 5 octane, decane, cyclohexane, decalin, butyl acetate and pentyl acetate, and a monomer which is used as a raw material of a polymer to be produced. Among these, a monomer, which is used as a raw material of a polymer to be produced, is used. The monomer, which is used as a raw 10 material of a polymer to be produced, is usually liquid. When the monomer is used as the solvent, it is possible to prevent impurities from mixing in the obtained polymer. Since the liquid contains a polymerization inhibitor, a polymerization reaction of the monomer as the solvent is 15 prevented even in the liquid.

[0023]

Examples of the polymerization inhibitor include hydroquinone, hydroquinone monomethyl ether, tert-butyl catechol, 4-methoxy-1-naphthol, 1,4-naphthoquinone, 2,4- 20 dimethyl-6-tert-butylphenol, phenothiazine, benzophenothiazine, dinitrobenzene, p-phenyldiamine, dimethyldithiocarbamic acid salt and the like. Among these polymerization inhibitors, 2,4-dimethyl-6-tert-butylphenol is preferred from the viewpoint of being less likely to 25 exert an adverse influence such as coloration even if it

remains in the polymer. The polymerization inhibitor to be used is appropriately selected according to the polymer to be produced, and the monomer to be used as a raw material thereof.

5 [0024]

The content of the polymerization inhibitor in the liquid is preferably from 5 to 2,000 ppm by mass, and more preferably from 10 to 500 ppm by mass, based on the entire liquid amount. When the content is more than the
10 aforementioned range, the proportion of the polymerization inhibitor contained in the polymer increases and thus the polymer may be slightly colored. In contrast, when the content is less than the aforementioned range, the effect of suppressing a polymerization reaction of an unreacted
15 monomer in the vicinity of shaft seal bearing portion 30 may decrease and also the effect of suppressing a polymerization reaction of the monomer may decrease when the monomer is used as the solvent.

[0001]

20 The flow rate of a liquid to be introduced is appropriately set according to the size, extrusion conditions and the like of the devolatilizing extruder, and is usually from 0.01 to 5 L/min, and preferably from 0.1 to 3 L/min, per one screw. When the flow rate of a liquid is
25 more than the aforementioned range, the proportion of the

polymerization inhibitor contained in the polymer increases and thus the polymer may be slightly colored. In contrast, when the flow rate is less than the aforementioned range, the effect of suppressing an unreacted monomer and a
5 polymer from penetrating into the shaft seal bearing portion 30 may decrease.

[0026]

In the devolatilizing extruder 100, the cavity
portion 34 is provided with the liquid introduction port 36
10 and the liquid is introduced, thereby enabling the interior of the cavity portion 34 to be in a pressurized state and enabling the pressure to be higher than that of the gas discharge port 14a of the devolatilizing extruder 100. Therefore, it is possible to sufficiently suppress an
15 unreacted monomer and a polymer from penetrate into the shaft seal bearing portion 30 through a flow path FP. The pressure within a preferred range in the cavity portion 34 is appropriately set according to the size, extrusion conditions and the like of the devolatilizing extruder, and
20 the pressure is made higher than that of the gas discharge port 14a of the devolatilizing extruder 100 and is also made lower than a filling pressure of the mechanical seal liquid 32c. It is preferred that a liquid delivery pump body is provided with a safety device such as a relief
25 valve so as to prevent the pressure from excessively

increasing. Also, since the devolatilizing extruder is provided with a pressure gauge and a safety valve according to a maximum working pressure, the pressure in cavity portion 34 is set so that the safety valve does not operate.

5 [0027]

The distance between an inner wall face of a through-hole 18 and a surface of a shaft portion 20a of a screw 20 is appropriately set according to the size, extrusion conditions and the like of the devolatilizing extruder, and is usually from 0.1 to 2.0 mm, and preferably from 0.1 to 1.5 mm. When this distance is more than the aforementioned range, the unreacted monomer and polymer may be likely to intrude into the flow path FP. In contrast, when the distance is less than the aforementioned range, it may become difficult to discharge the liquid introduced into the cavity portion 34 into the cylinder 10 and thus the effect of suppressing the polymer of the unreacted monomer from adhering in the vicinity of shaft seal bearing portion 30 may decrease.

20 [0028]

In the devolatilizing extruder 100, the polymer composition is supplied from the polymer composition supply port 12. At this time, a liquid polymer composition is converted into a vapor mist by adjusting the pressure in the vicinity of the polymer composition supply port 12, and

at least a part of the volatile component contained in the polymer composition is discharged through gas discharge ports 14a, 14b close to the polymer composition supply port 12. The liquid, that is introduced through the liquid introduction port 36 and pass through the cavity portion 34 and then discharged in the cylinder 10 through the flow path FP, is mainly discharged through a gas discharge port (back vent) 14a, together with a part of the volatile component. The polymer composition goes forward to the side of the polymer outlet 16 by rotation of the screw 20 and most of the volatile component contained in the polymer composition is vaporized until the polymer composition reaches the polymer outlet 16, and then discharged through gas discharge ports 14b, 14c, 14d. In addition to the unreacted monomer, a solvent and additives being used optionally and a volatile by-product being produced during the polymerization process are contained in the volatile component that is discharged through the gas discharge port 14. Thus, it is possible to obtain a devolatilized polymer through the polymer outlet 16, from which most of the volatile component has been removed. The polymer can be obtained, for example, in the form of pellets.

[0029]

The aforementioned devolatilizing extruder 100 can be suitably used to produce a (meth)acrylic polymer that is

obtained by polymerizing a monomer mixture containing methyl (meth)acrylate as a main component among polymers.

[0030]

In the devolatilizing extruder 100, there is no particular limitation on the number of gas discharge ports 14 formed in the cylinder 10. While the constriction in which four gas discharge ports 14 are provided was described in Fig. 1, the number of gas discharge ports 14 may be from 1 to 3, or 5 or more. From the viewpoint of efficiently discharging the liquid introduced through the liquid introduction port 36 and the volatile component in the polymer composition, the cylinder 10 preferably includes one or more of gas discharge ports (back vents) provided between the polymer composition supply port 12 and the shaft seal bearing portion 30, and one or more of gas discharge ports (fore vents) provided between the polymer composition supply port 12 and the polymer outlet 16, and more preferably one back vent and one to three fore vent.

[0031]

There is no particular limitation on the number of screws 20 used in the devolatilizing extruder 100. The number of screws is preferably one to two, and more preferably two. A twin-screw devolatilizing extruder including two screws 20 is preferred since a (meth)acrylic polymer can be efficiently produced. There is no

particular limitation on the diameter of the screw 20, and is usually from $\phi 100$ to 450 mm.

[0032]

The method for devolatilizing extrusion of a polymer composition and the method for producing a polymer of the present invention will be described below.

[0033]

The method for producing a polymer of the present invention is a method comprising a step of continuously supplying a raw material containing a monomer, a radical polymerization initiator and a chain transfer agent into a polymerization reaction vessel; a step of polymerizing the monomer in the polymerization reaction vessel to obtain a polymer composition containing a polymer and a volatile component containing an unreacted monomer; and a step of supplying the polymer composition into a cylinder through a polymer composition supply port in the devolatilizing extruder of the present invention, and also supplying a liquid containing a polymerization inhibitor to a cavity portion through a liquid introduction port, and to discharge the volatile component through the gas discharge port and to discharge the polymer after devolatilization through a polymer outlet , respectively. The respective steps will be described in detail below.

[0034]

Fig. 3 is a schematic block diagram showing a production system of a polymer. As shown in Fig. 3, first, an initiator composition and a monomer composition are blended in an initiator blending vessel 101 and a monomer blending vessel 102, respectively. The initiator composition is prepared by mixing a radical polymerization initiator, a monomer and a chain transfer agent. The monomer composition is prepared by mixing a monomer and a chain transfer agent. Then, the blended initiator composition and monomer composition are continuously supplied to a polymerization reaction vessel 103, where a polymerization reaction is carried out.

[0035]

Herein, the monomer, the radical polymerization initiator and the chain transfer agent are selected according to a polymer to be produced. The case where a (meth)acrylic polymer such as polymethyl methacrylate is produced will be described below as preferred embodiment. In the present description, "(meth)acryl" means "acryl" and "methacryl" corresponding thereto.

[0036]

There is no particular limitation on the monomer used as a raw material of a (meth)acrylic polymer. Examples thereof include an alkyl (meth)acrylate alone (an alkyl group having 1 to 4 carbon atoms) alone, or a mixture of

not less than 80% by mass of an alkyl (meth)acrylate (an alkyl group having 1 to 4 carbon atoms) and not more than 20% by mass of the other vinyl monomer that is copolymerizable with the alkyl (meth)acrylate. Examples of the alkyl of the alkyl (meth)acrylate (an alkyl group having 1 to 4 carbon atoms) include methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl and the like and, among alkyl (meth)acrylates, methyl (meth)acrylate is preferred.

[0037]

Examples of the copolymerizable vinyl monomer include (meth)acrylate other than the alkyl (meth)acrylate (an alkyl group having 1 to 4 carbon atoms), such as benzyl (meth)acrylate and 2-ethylhexyl (meth)acrylate; unsaturated carboxylic acids or acid anhydrides thereof, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, maleic anhydride and itaconic anhydride; hydroxyl group-containing monomers such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, monoglycerol acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate and monoglycerol methacrylate; nitrogen-containing monomers such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, diacetoneacrylamide and dimethylaminoethyl methacrylate; epoxy group-containing monomers such as allyl glycidyl ether, glycidyl acrylate and glycidyl methacrylate; and styrenic monomers such as

styrene and α -methylstyrene.

[0038]

When the present invention is applied to the production of (meth)acrylate-based polymer, examples of the polymerization initiator to be supplied to a reaction vessel include a radical polymerization initiator. Examples of the radical polymerization initiator include azo compounds such as azobisisobutyronitrile, azobisdimethylvaleronitrile, azobiscyclohexanenitrile, 1,1'-azobis(1-acetoxy-1-phenylethane), dimethyl 2,2'-azobisisobutylate and 4,4'-azobis-4-cyanovaleric acid; and organic peroxides such as benzoyl peroxide, lauroyl peroxide, acetyl peroxide, capryl peroxide, 2,4-dichlorobenzoyl peroxide, isobutyl peroxide, acetylcyclohexylsulfonyl peroxide, t-butyl peroxy-pivalate, t-butylperoxy-2-ethyl hexanoate, 1,1-di-t-butylperoxycyclohexane, 1,1-di-t-butylperoxy-3,3,5-trimethylcyclohexane, 1,1-di-t-hexylperoxy-3,3,5-trimethylcyclohexane, isopropyl peroxydicarbonate, isobutyl peroxydicarbonate, s-butyl peroxydicarbonate, n-butyl peroxydicarbonate, 2-ethylhexyl peroxydicarbonate, bis(4-t-butylcyclohexyl) peroxydicarbonate, t-amylperoxy-2-ethyl hexanoate, 1,1,3,3-tetramethylbutyl peroxy-ethyl hexanoate, 1,1,2-trimethylpropyl peroxy-2-ethylhexanoate, t-butyl peroxyisopropyl monocarbonate, t-amyl peroxyisopropyl

monocarbonate, t-butyl peroxy-2-ethyl hexylcarbonate, t-butyl peroxyallyl carbonate, t-butyl peroxyisopropyl carbonate, 1,1,3,3-tetramethylbutyl peroxyisopropyl monocarbonate, 1,1,2-trimethylpropyl peroxyisopropyl
5 monocarbonate, 1,1,3,3-tetramethylbutyl peroxyisononanoate, 1,1,2-trimethylpropyl peroxyisononanoate and t-butyl peroxybenzoate. These polymerization initiators may be used alone, or a mixture of two or more kinds may be used.
[0039]

10 There is no particular limitation on the blend amount of the radical polymerization initiator, and the blend amount is usually from 0.001 to 1 part by mass based on 100 parts by mass of the monomer as a raw material. When a mixture of two or more kinds of radical polymerization
15 initiators is used, the total used amount may be within this range. The polymerization initiator supplied into the reaction vessel is selected according to the polymer to be produced and the kind of a raw monomer used and is not particularly limited in the present invention. For example,
20 the radical polymerization initiator is preferably a radical polymerization initiator in which a half-life at a polymerization temperature is within 1 minute. When the half-life at the polymerization temperature is more than 1 minute, the reaction rate decreased, and thus the radical
25 polymerization initiator may be unsuited for the

polymerization reaction in a continuous polymerization device. A relationship between the temperature of the radical polymerization initiator and the half-life is described in various documents and technical data of
5 manufacturers for each kind of the radical polymerization initiator. In the present invention, values described in a known products catalog of Wako Pure Chemical Industries, Ltd., KAYAKU AKZO CO., LTD. or the like were used.

[0040]

10 When the present invention is applied to the production of a (meth)acrylate-based polymer, a chain transfer agent can be blended in a reaction vessel so as to adjust the molecular weight of the polymer to be produced. The chain transfer agent may be either a monofunctional or
15 polyfunctional chain transfer agent. Specific examples thereof include alkylmercaptans such as propylmercaptan, butylmercaptan, hexylmercaptan, octylmercaptan, 2-ethylhexylmercaptan and dodecylmercaptan; aromatic mercaptans such as phenylmercaptan and thiocresol;
20 mercaptans having not more than 18 carbon atoms, such as ethylene thioglycol; polyhydric alcohols such as ethylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol; those obtained by esterifying a hydroxyl group
25 with thioglycolic acid or 3-mercaptopropionic acid, 1,4-

dihydronaphthalene, 1,4,5,8-tetrahydronaphthalene, β -terpinene, terpinolene, 1,4-cyclohexadiene, 1,4-cyclohexadiene, hydrogen sulfide and the like. These chain transfer agents may be used alone, or two or more
5 kinds may be used in combination.

[0041]

Since the blend amount of the chain transfer agent varies depending on the kind of the chain transfer agent used and the like, there is no particular limitation on the
10 blend amount. For example, when mercaptans are used, the blend amount is preferably from 0.01 to 3 parts by mass, and more preferably from 0.05 to 1 part by mass, based on 100 parts by mass of the monomer as a raw material. The use amount within this range is preferred since
15 thermostability is satisfactorily maintained without impairing mechanical properties of the polymer. When two or more kinds of chain transfer agents are used in combination, the total use amount may be adjusted within this range.

20 [0042]

A polymerization reaction vessel 103 used in the present embodiment is a vessel type reactor equipped with a stirrer. The stirrer enables a solution in a vessel to convert into a substantially completely mixed state. It is
25 possible to use, as a stirring impeller, a Maxblend

impeller manufactured by Sumitomo Heavy Industries, Ltd., a paddle impeller, a double helical ribbon impeller, an MIG impeller, a full zone impeller manufactured by Shinko Pantech Co Ltd. and the like, however, there is no particular limitation. It is preferred to attach a baffle so as to increase the stirring effect.

[0043]

As a matter of course, it is preferred that the stirring efficiency is as high as possible. The stirring power that is more than the necessity is not preferred since only surplus heat is applied to a reaction vessel. Therefore, the stirring power is from 0.5 to 20 kW/m³, and preferably from 1 to 15 kW/m³. It is necessary that this stirring power is increased as the viscosity of a content liquid, namely, the content of the polymer becomes larger.

[0044]

The polymerization reaction vessel 103 is preferably in a state of being filled with a liquid, which is substantially free from a vapor phase. When the polymerization reaction vessel is in a state of being filled with a liquid, adhesion and production of the polymer on a vapor phase portion and a vessel inner wall face as a gas-liquid interface are suppressed, and thus deterioration in quality due to mixing of them in the product can be suppressed. Moreover, since the entire

volume of the polymerization reaction vessel 103 can be effectively utilized, productivity can be improved.

[0045]

In order to fill the polymerization reaction vessel 103 with a liquid, it is most simple to dispose an outlet of a solution in a vessel on the top portion of a reaction vessel. In this case, a supply port of a raw material (an initiator composition and a monomer composition) is preferably provided at the lower portion of the polymerization reaction vessel 103. It is desired to prevent a gas of a monomer from generating in the polymerization reaction vessel 103. For that purpose, it is preferred to adjust the pressure in the vessel to a vapor pressure or more at a temperature of a content liquid. This pressure is generally from about 10 to 20 kg/cm².

[0046]

The interior of the polymerization reaction vessel 103 is preferably in an insulated state that is substantially free from inflow/outflow of heat from the outside. Namely, it is preferred to adjust the temperature in the reaction vessel and the temperature on the side of the reaction vessel outer wall face to about the same temperature. Specifically, a jacket is disposed, for example, at the side of the reaction vessel outer wall face and the temperature of the reaction vessel outer wall is

allowed to follow the temperature in the reaction vessel using steam, other heat medium or the like, and thus nearly the same temperature can be achieved.

[0047]

5 The polymerization reaction vessel 103 is kept in an insulated state since a formation of a polymer on the reaction vessel inner wall face can be prevented and self-controllability of being capable of suppressing a runaway reaction by stabilizing the polymerization reaction is
10 imparted. It is not preferred to adjust the temperature of the reaction vessel inner wall face to a temperature that is excessively higher than that of the content liquid since surplus heat is applied to the interior of the reaction vessel. It is preferred that a temperature difference
15 between the interior of the reaction vessel and the reaction vessel outer wall is as small as possible. However, the temperature may be actually adjusted to a variation within a range of about $\pm 5^{\circ}\text{C}$.

[0048]

20 In the present embodiment, heat generated in the polymerization reaction vessel 103, namely, polymerization heat and stirring heat is preferably well-balanced with quantity of heat taken by a liquid (syrup-like) polymer composition that is discharged from the polymerization
25 reaction vessel 103. Quantity of heat taken by the polymer

composition is determined by the amount, specific heat and temperature (polymerization temperature) of the polymer composition.

[0049]

5 The polymerization temperature varies depending on the kind of the radical polymerization initiator used and is preferably from about 120 to 180°C, and more preferably from 130 to 180°C. When this temperature is too high, the obtained polymer exhibits low syndiotacticity, and thus the
10 amount of oligomer produced may increase and heat resistance of the resin may deteriorate.

[0050]

 The average residence time in the polymerization reaction vessel 103 is preferably not less than 15 minutes
15 nor more than 2 hours, and more preferably not less than 20 minutes nor more than 1.5 hours. When the average residence time is longer than the necessity, the amount of an oligomer such as dimer or trimer produced increases and thus heat resistance of the product may deteriorate. The
20 average residence time can be adjusted by changing the supply amount of the monomer per unit time.

[0051]

 It is possible to use, as the initiator blending vessel 101 and the monomer blending vessel 102 used in the
25 present embodiment, a blending vessel equipped with the

same stirrer as that of the aforementioned polymerization reaction vessel 103. In the initiator blending vessel 101, a radical polymerization initiator is completely dissolved in a monomer to obtain an initiator solution. The
5 temperature in the initiator blending vessel 101 is maintained at a temperature at which a polymerization reaction does not proceed, and preferably maintained at -20 to 10°C. In contrast, the temperature in the monomer blending vessel 102 is maintained at a temperature at which
10 the monomer is not volatilized, and is preferably maintained at -20 to 10°C. An initiator composition and a monomer composition as raw materials of the polymer are continuously supplied into the polymerization reaction vessel 103 from the initiator blending vessel 101 and the
15 monomer blending vessel 102 by a pump or the like.

[0052]

The amount of the initiator composition supplied from the initiator blending vessel 101 to the polymerization reaction vessel 103 varies depending on the capacity or the
20 like of the polymerization reaction vessel 103 and the amount is, for example, preferably from 0.1 to 10 kg/hr, and more preferably from 0.5 to 5 kg/hr, when the capacity of the polymerization reaction vessel 103 is 10 L. The amount of the monomer composition supplied from the monomer
25 blending vessel 102 to the polymerization reaction vessel

103 varies dependg on the capacity or the like of the
polymerization reaction vessel 103 and the amount is, for
example, preferably from 4 to 40 kg/hr, and more preferably
from 10 to 30 kg/hr, when the capacity of the
5 polymerization reaction vessel 103 is 10 L.

[0053]

There may be used, as the monomer blended in the
monomer blending vessel 102, not only a fresh monomer, but
also a monomer separated and recovered in an unreacted
10 state as shown in Fig. 3. When the monomer is blended, it
is common that an inert gas is bubbled into the monomer
blending vessel 102 or dissolved oxygen is removed by
pressure reducing deaeration, so as to prevent an influence
by dissolved oxygen. In the method of the present
15 embodiment, it is not necessarily required to strictly
remove dissolved oxygen, and a polymerization reaction can
be stably carried out even though about 1.5 to 3 ppm of
dissolved oxygen exist. When the blended monomer
composition is supplied into the polymerization reaction
20 vessel 103, it is particularly preferred to filter with a
filter having an appropriate size selected according to the
purposes so as to remove foreign matters in the case of
using the obtained polymer in the material for an optical
equipment.

25 [0054]

In the method for producing a polymer of the present embodiment, as described above, an initiator composition and a monomer composition as raw materials of the polymer are continuously supplied into the polymerization reaction vessel 103 from the initiator blending vessel 101 and the monomer blending vessel 102, and then at least a part of a monomer is polymerized in the polymerization reaction vessel 103 to obtain a polymer composition containing the polymer and the unreacted monomer. In the polymerization reaction vessel 103, a polymerization method of the polymer may be either a bulk polymerization using no solvent or a solution polymerization using a solvent, and a bulk polymerization method is particularly preferred.

[0055]

The polymerization is carried out by a continuous solution polymerization method in the same manner as in the aforementioned continuous bulk polymerization method, except that the solvent is used in the polymerization reaction. The solvent used in the polymerization reaction may be appropriately set according to a raw monomer of the continuous solution polymerization reaction or the like and is not particularly limited, and examples thereof include toluene, xylene, ethylbenzene, methyl isobutyl ketone, methyl alcohol, ethyl alcohol, octane, decane, cyclohexane, decalin, butyl acetate, pentyl acetate and the like. Among

these solvents, toluene, methanol, ethylbenzene and butyl acetate are preferred. The solvent can be added to one or both of an initiator composition and a monomer composition. There is no particular limitation on the proportion of the solvent, and the proportion is preferably from 5 to 30% by mass, and more preferably from 1 to 20% by mass, based on the entire polymer composition.

[0056]

The content of the polymer in the polymer composition is preferably from 40 to 70% by mass. When the content of the polymer is too high, efficiency of mixing and heat transfer may decrease and thus stability may become worse. In contrast, when the content of the polymer is too low, it may become difficult to separate a volatile component containing an unreacted monomer as a main component.

[0057]

The polymer composition produced in the polymerization reaction vessel 103 is continuously extracted from the polymerization reaction vessel 103 and then optionally lead to a heater 104. In the heater 104, a liquid polymer composition is preheated for the purpose of increasing efficiency of subsequent devolatilization in a devolatilizing extruder 100. At this time, the preheating temperature is preferably adjusted within a range of 180 to 220°C. When the preheating temperature is higher than the

aforementioned range, a volatile component may be gasified and thus it may become difficult to deliver a liquid at a given flow rate.

[0058]

5 Next, the polymer composition is supplied to the devolatilizing extruder 100. As the devolatilizing extruder 100, the aforementioned devolatilizing extruder 100 of the present invention is used. The devolatilizing extrusion is carried out by continuously supplying a
10 polymer composition into a cylinder 10 through a polymer composition supply port 12 in the devolatilizing extruder 100, and also supplying a liquid containing the polymerization inhibitor to a cavity portion 34 through a liquid introduction port 36 to discharge a volatile
15 component containing an unreacted monomer as a main component through a gas discharge port 14 and to discharge a polymer after devolatilization through a polymer outlet 16, respectively. The kind and the flow rate of the liquid to be supplied are as described previously.

20 [0059]

 The devolatilizing extrusion is carried out by heating a polymer composition to be continuously supplied at 200 to 290°C thereby continuously separating and removing most of the volatile component containing an
25 unreacted monomer as a main component. With respect to the

pressure condition at the time of devolatilizing extrusion,
the pressure of a gas discharge port (back vent) 14a is
adjusted within a range of about -0.05 to 0.15 MPaG (in
terms of gauge pressure) and the pressures of gas discharge
5 ports (fore vents) 14b, 14c, 14d are respectively adjusted
within a range of about -0.09 to -0.02 MPaG (in terms of
gauge pressure). The gasified volatile component and
polymer enter into the devolatilizing extruder 100 through
the polymer composition supply port 12. At this time, when
10 the pressure of the back vent is decreased to -0.05 MPaG,
an entrainment phenomenon arises at the back vent, and thus
it is preferred to adjust the pressure within the
aforementioned range. In order to remove the volatile
component, the pressures of four vents are preferably
15 adjusted within the aforementioned range. Usually, a
pressure regulating valve is disposed between the heater
104 and the devolatilizing extruder 100, thereby adjusting
the pressure at the time of devolatilizing extrusion.

[0060]

20 On or after the aforementioned devolatilizing
extrusion, lubricants such as higher alcohols and higher
fatty acid esters, an ultraviolet absorber, a heat
stabilizer, a coloring agent, an antistatic agent and the
like can be added to the polymer.

25 [0061]

The volatile component containing an unreacted monomer as a main component discharged through the gas discharge port 14 is sent to a monomer recovery tower 105. The volatile component containing an unreacted monomer as a main component contains impurities contained originally in a monomer, oligomers such as a dimer and a trimer, and impurities such as a radical polymerization initiator residue. When the polymerization is carried out by the continuous solution polymerization method, a solvent can be contained in addition to these impurities. When impurities are accumulated, the obtained polymer undergoes coloration. Therefore, impurities are removed from the unreacted monomer by a means such as distillation or adsorption in the monomer recovery tower 105, and then the obtained monomer is recycled as a monomer for polymerization. For example, in the monomer recovery tower 105, the monomer is recovered as a distillatory solution from a tower top of the monomer recovery tower 105 by continuous distillation, and then recycled to the monomer blending vessel 102. Impurities removed in the monomer recovery tower 105 are discarded as wastes. The volatile component containing an unreacted monomer as a main component usually refers to those in which not less than 30% by mass of the unreacted monomer is contained in the volatile component.

[0062]

In the method for devolatilizing extrusion of a polymer composition and the method for producing a polymer described above, it is possible to sufficiently suppress an unreacted monomer, a polymer thereof and the like from adhering in the vicinity of shaft seal bearing portion of the devolatilizing extruder, and thus a polymer can be continuously produced over a long period without causing a problem such as poor rotation of a screw.

[0063]

10 The aforementioned method for devolatilizing extrusion of a polymer composition and method for producing a polymer can be suitably used in the production of a (meth)acrylic polymer among polymers, and can be particularly suitably used in the production of a (meth)acrylic polymer obtained by polymerizing a monomer mixture containing methyl (meth)acrylate as a main component.

[0064]

20 The polymer such as a (meth)acrylic polymer obtained by the aforementioned method can be suitably in various fields such as illuminations, signboards and vehicles since excellent transparency and weatherability can be obtained. The (meth)acrylic polymer can be used particularly suitably in materials for an optical disk substrate; materials for an optical equipment such as Fresnel lens, lenticular lens,

25

a light guide plate and a diffuser panel used in a backlight system of a liquid crystal display, and a protective front panel of a liquid crystal display; vehicle members such as a tail lamp cover, a head lamp cover, a visor and a meter panel; and the like.

Description of Reference Symbols

[0065]

- 10: Cylinder
- 12: Polymer composition supply port
- 10 14: Gas discharge port
- 16: Polymer outlet
- 18: Through-hole
- 20: Screw
- 20a: Shaft portion
- 15 30: Shaft seal bearing portion
- 32: Shaft seal portion
- 34: Cavity portion
- 36: Liquid introduction port
- 100: Devolatilizing extruder

CLAIMS

1. A devolatilizing extruder comprising:
 - a cylinder having a polymer composition supply port,
 - 5 a gas discharge port, a polymer outlet and a through-hole;
 - a rotatable screw inserted into the cylinder through the through-hole; and
 - a shaft seal bearing portion supporting a shaft portion of the screw extending from the through-hole to the
 - 10 outside of the cylinder; wherein
 - the shaft seal bearing portion includes a shaft seal portion, a cavity portion formed between the shaft seal portion and the cylinder, and a liquid introduction port for introducing a liquid containing a polymerization
 - 15 inhibitor into the cavity portion, and also
 - the shaft seal bearing portion has a gap serving as a flow path, through which a liquid introduced into the cavity portion through the liquid introduction port is discharged into the cylinder, between an inner wall face of
 - 20 the through-hole and a surface of the shaft portion of the screw.
2. The devolatilizing extruder according to claim 1, wherein the shaft seal portion is formed of a mechanical
- 25 seal.

3. A method for devolatilizing extrusion of a polymer composition, comprising: supplying a polymer composition containing a polymer and a volatile component into a cylinder through a polymer composition supply port in the devolatilizing extruder according to claim 1 or 2 and also supplying a liquid to the cavity portion through the liquid introduction port to discharge the volatile component through the gas discharge port and to discharge a polymer after devolatilization through the polymer outlet, respectively.

4. The method for devolatilizing extrusion of a polymer composition according to claim 3, wherein the liquid is a liquid prepared by dissolving the polymerization inhibitor in a monomer used as a raw material of the polymer.

5. A method for producing a polymer, comprising the steps of:

continuously supplying a raw material containing a monomer, a radical polymerization initiator and a chain transfer agent into a polymerization reaction vessel;

polymerizing the monomer in the polymerization reaction vessel to obtain a polymer composition containing a polymer and a volatile component containing an unreacted

monomer; and

supplying the polymer composition into the cylinder through the polymer composition supply port in the devolatilizing extruder according to claim 1 or 2 and also supplying a liquid to the cavity portion through the liquid introduction port to discharge the volatile component through the gas discharge port and to discharge a polymer after devolatilization through the polymer outlet, respectively.

6. The method for producing a polymer according to claim 5, wherein the liquid is a liquid prepared by dissolving the polymerization inhibitor in the monomer.