

Description

PROCESS OF MANUFACTURING A POLYCARBONATE RESIN PELLETT AND
MOLDED ARTICLE

5

Technical Field

The present invention relates to a process of manufacturing a polycarbonate resin pellet which is advantageously used as a material for storage and transport
10 containers for silicon wafers or magnetic disks and a molded article thereof.

Background of the Art

In general, it is important that a container for storing
15 and carrying thin plates sensitive to surface contamination such as silicon wafers or magnetic disks should be able to carry a silicon wafer while its surface is always kept in a normal state.

Since the requirements against the contamination of
20 the surface of a wafer from a container are becoming more strict along with an increase in the diameter of a silicon wafer, a material having higher strength is desired. There are same requirements for containers for storing and carrying magnetic disks like wafers. Attempts are being made to use
25 a polycarbonate resin or a resin composition comprising the polycarbonate resin as the main component as a molding material which meets the above requirements.

For example, Patent Documents 1 to 4 disclose a method of preventing the contamination of the surface of a silicon
30 wafer by removing impurities contained in a polycarbonate resin or reducing the amount of a volatile gas generated by heating at a high temperature. Since a container for storing and carrying silicon wafers or magnetic disks is not used only once but used repeatedly by washing in water, the storage

and transport container disclosed by Patent Document 1 to 4 has a problem that ionic impurities are eluted by washing in water and ionic impurities adhered to the surface of the container contaminate the surface of a wafer or the like.

5 Meanwhile, there is proposed a method of removing impurities contained in a polycarbonate resin by injecting water at the time of melt extrusion. Patent Documents 5 to 7 propose a method of extruding a polycarbonate resin powder with a vented extruder while a small amount of water is
10 injected. Although impurities contained in the polycarbonate resin and a chlorine compound can be removed to a certain extent in the method, the polycarbonate resin powder is not satisfactory as a material for the above-described container for storing and carrying wafers.

15 (patent document 1) JP-A 10-211686
 (patent document 2) JP-A 11-241012
 (patent document 3) WO2000/043436
 (patent document 4) JP-A 2000-063505
 (patent document 5) JP-B 05-048162
20 (patent document 6) JP-B 07-002364
 (patent document 7) JP-A 09-193230

Disclosure of the Invention

25 It is an object of the present invention to provide a process of manufacturing a polycarbonate resin which has a low content of a chlorine atom and a small amount of an eluted chlorine ion. It is another object of the present invention to provide a process of manufacturing a polycarbonate resin suitable for use as a material for
30 storage and transport containers which rarely contaminate the surface of a thin plate sensitive to surface contamination, such as a silicon wafer or a magnetic disk. It is still another object of the present invention to provide a molded article such as a storage and transport container

which rarely contaminates the surface of its content.

The inventors of the present invention have conducted intensive studies to attain the above objects. As a result, they have found that the deaeration efficiency is improved
5 by deaerating a polycarbonate resin with a vent after the polycarbonate resin is kneaded efficiently and water is dispersed in and mixed with the polycarbonate resin by providing a special structure to the screw constitution of a double-screw extruder to increase kneading performance
10 right after the inlet of water, thereby making it possible to obtain a polycarbonate resin pellet having a low content of a chlorine compound. They have also found that a molded article obtained from the pellet has a small amount of the generated chlorine atom even when it is washed in water and
15 therefore can be advantageously used as a storage and transport container for silicon wafers or magnetic disks. The present invention is accomplished based on these findings.

That is, according to the present invention, there is
20 provided a process of manufacturing a pellet by melt extruding a polycarbonate resin powder from a double-screw extruder, wherein

(i) the double-screw extruder has at least one kneading/extrusion unit which comprises a water inlet part,
25 a kneading part right below the water inlet part, a seal ring located on the upstream side, downstream side or both sides of the kneading part and a vent part on the downstream side of the water inlet part;

(ii) a screw element at the most upstream of the kneading part is an orthogonal kneading disk (c) or a forward
30 kneading disk (f) and a screw element at the most downstream is a backward kneading disk (r);

(iii) the length (L_1) of each screw element of the kneading part is $0.25D$ to D , and the length (L_2) of the

kneading part is D to 4D (D is the inner diameter of a cylinder); and

water is injected from the water inlet part (W) and the vacuum degree of the vent part (V) is set to 6.7 kPa or less.

According to the present invention, there is provided a molded article formed from the polycarbonate resin pellet obtained by the above manufacturing process.

The present invention will be described in detail hereinunder.

Brief Description of the Drawings

Fig. 1 is a diagram showing the structure of a double-screw extruder used in the present invention;

Fig. 2 is a diagram showing the structure of a double-screw extruder used in Examples (screw A);

Fig. 3 is a diagram showing the structure of a double-screw extruder used in Examples (screw B);

Fig. 4 is a diagram showing the structure of a double-screw extruder used in Examples (screw C);

Fig. 5 is a diagram showing the structure of a double-screw extruder used in Examples (screw D);

Fig. 6 is a diagram showing the structure of a double-screw extruder used in Example (screw E); and

Fig. 7 is a diagram showing the structure of a double-screw extruder used in Example (screw F).

Explanation of Letters or Notations

1. water inlet part
2. kneading part
3. seal ring
4. vent part
5. auxiliary vent part
6. additive introduction part

Best Mode for Carrying Out the Invention
(polycarbonate resin)

The polycarbonate resin used in the present invention
 5 is an aromatic polycarbonate resin obtained by reacting a
 diphenol with a carbonate precursor in the presence of a
 solvent by an interfacial polymerization process. Examples
 of the diphenol used herein include hydroquinone, resorcinol,
 4,4'-dihydroxydiphenyl, bis(4-hydroxyphenyl)methane,
 10 1,1-bis(4-hydroxyphenyl)ethane,
 2,2-bis(4-hydroxyphenyl)propane (commonly called
 "bisphenol A"), 2,2-bis(3-methyl-4-hydroxyphenyl)propane,
 1,1-bis(4-hydroxyphenyl)cyclohexane (commonly called
 "bisphenol Z"), 2,2-bis(3-phenyl-4-hydroxyphenyl)propane,
 15 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane,
 2,2-bis(4-hydroxyphenyl)butane,
 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane,
 4,4'-dihydroxydiphenylsulfone,
 4,4'-dihydroxydiphenylsulfoxide,
 20 4,4'-dihydroxydiphenylsulfide,
 3,3'-dimethyl-4,4'-dihydroxydiphenylsulfide,
 4,4'-dihydroxydiphenyl oxide,
 9,9-bis(4-hydroxyphenyl)fluorene,
 9,9-bis{(4-hydroxy-3-methyl)phenyl}fluorene,
 25 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane,
 α,α' -bis(4-hydroxyphenyl)-m-diisopropylbenzene and
 1,3-bis(4-hydroxyphenyl)-5,7-dimethyladamantane. Out of
 these, bisphenol A, bisphenol Z,
 9,9-bis{(4-hydroxy-3-methyl)phenyl}fluorene,
 30 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane and
 α,α' -bis(4-hydroxyphenyl)-m-diisopropylbenzene are
 particularly preferred. They may be used alone or in
 combination of two or more.

The carbonate precursor is a carbonyl halide or

haloformate, as exemplified by phosgene and dihaloformates of a diphenol.

For the manufacture of the polycarbonate resin by reacting the above diphenol with the above carbonate precursor by the interfacial polycondensation process, a terminal capping agent and an antioxidant for preventing the oxidation of the diphenol may be optionally used. The polycarbonate resin may be a branched polycarbonate resin obtained by copolymerizing a polyfunctional aromatic compound having 3 or more functional groups, a polyester carbonate resin obtained by copolymerizing an aromatic or aliphatic bifunctional carboxylic acid, or a mixture of two or more of the obtained aromatic polycarbonate resins.

The reaction by the interfacial polycondensation process is generally a reaction between a diphenol and phosgene in the presence of an acid binder, a catalyst and an organic solvent.

Examples of the acid binder include alkali metal hydroxides such as sodium hydroxide and potassium hydroxide and amine compounds such as pyridine.

Examples of the organic solvent include halogenated hydrocarbons such as methylene chloride, chloroform, 1,2-dichloroethane, 1,1-dichloroethane, bromoethane, butyl chloride, chloropropane and chlorobenzene. Out of these, methylene chloride is particularly preferred. These solvents may be used alone or in combination of two or more.

Examples of the amine-based catalyst used to promote the reaction include tertiary amines such as triethylamine, tetra-n-butylammonium bromide and tetra-n-butylphosphonium bromide, quaternary ammonium compounds and quaternary phosphonium compounds. Out of these, triethylamine is particularly preferably used.

The temperature of the reaction by the interfacial polycondensation process is generally 0 to 40°C, the reaction

time is about 10 minutes to 5 hours, and pH during the reaction is preferably kept at 9 or more.

In the polymerization reaction, a terminal capping agent is generally used. A monofunctional phenol may be used
 5 as the terminal capping agent. The monofunctional phenol is generally used as the terminal capping agent to control the molecular weight, and the obtained polycarbonate resin is superior in heat stability because its terminal is capped by a group based on the monofunctional phenol. Examples of
 10 the monofunctional phenol include phenol, p-tert-butylphenol, p-cumylphenol and isooctylphenol.

It is desired that the terminal capping agent should be introduced into the terminal in an amount of at least 5 mol%, preferably at least 10 mol% based on the total of all
 15 the terminals of the obtained polycarbonate resin. The terminal capping agents may be used alone or in combination of two or more.

The molecular weight of the polycarbonate resin is preferably 1×10^4 to 4×10^4 , more preferably 1.3×10^4 to
 20 3×10^4 , particularly preferably 1.6×10^4 to 2.4×10^4 in terms of viscosity average molecular weight (M). A polycarbonate resin having the above viscosity average molecular weight has satisfactory strength and excellent melt fluidity at the time of molding and is free from molding
 25 distortion. The viscosity average molecular weight is obtained by inserting the specific viscosity (η_{sp}) of a solution prepared by dissolving 0.7 g of the polycarbonate resin in 100 ml of methylene chloride at 20°C into the following equation.

30 $\eta_{sp}/c = [\eta] + 0.45 \times [\eta]^2 c$ ($[\eta]$ represents an intrinsic viscosity)

$$[\eta] = 1.23 \times 10^{-4} M^{0.83}$$

$$c = 0.7$$

The organic solvent solution of the polycarbonate

resin obtained by the above reaction is generally washed in water. This washing step is carried out by using water having an electric conductivity of 10 $\mu\text{S}/\text{cm}$ or less, more preferably 1 $\mu\text{S}/\text{cm}$ or less such as ion exchange water. The above organic solvent solution and water are mixed together, stirred and divided into an organic solvent solution phase and a water phase by still standing or using a centrifugal separator to extract the organic solvent solution phase repeatedly so as to remove water-soluble impurities. The water-soluble impurities are removed efficiently by washing in water, whereby the color of the obtained polycarbonate resin becomes good.

It is also preferred that the organic solvent solution of the polycarbonate resin should be washed with an acid or alkali to remove impurities such as the catalyst.

The acid used for acid washing is preferably an aqueous solution of phosphoric acid, hydrochloric acid or sulfuric acid, more preferably an aqueous solution having a concentration of 0.0004 to 40 g/liter (or a pH of 5 or less). Examples of the alkali used for alkali washing include alkali metal compounds such as sodium hydroxide and potassium hydroxide, and alkali earth metal compounds such as calcium hydroxide, barium hydroxide and magnesium hydroxide. Sodium hydroxide is particularly preferably used, and an aqueous solution having a concentration of 0.1 to 20 g/liter (or a pH of 11.5 or more) is preferably used.

The volume ratio of the aqueous solution to the organic solvent solution used for alkali washing or acid washing is preferably 0.2 to 1.5 because washing is carried out efficiently.

The solvent is removed from the organic solvent solution which has been washed in water to obtain a polycarbonate resin powder.

To obtain the polycarbonate resin powder (granulation

step), a method of producing slurry by continuously supplying the organic solvent solution of the polycarbonate resin into a granulator in which a polycarbonate powder and hot water (about 40 to 90°C) are existent under agitation to evaporate the solvent is preferably employed as it is simple in operation and post-treatment. A mixer such as a stirring tank or kneader is preferably used as the granulator.

The slurry may be subjected to a hydrothermal treatment. In the hydrothermal treatment step, the organic solvent contained in the slurry is removed by supplying the slurry into a hydrothermal treatment container filled with 90 to 100°C hot water or setting the temperature of water to 90 to 100°C by blowing steam after the slurry is supplied.

Water and the organic solvent are then removed to a certain extent from the slurry discharged from the granulating step or from the slurry after the hydrothermal treatment preferably by filtration or centrifugation so as to collect wet paste of the polycarbonate resin.

The wet paste of the polycarbonate resin is then dried. The drier may be of conduction heating system or hot air heating system, and the polycarbonate resin may be left to stand, transferred or stirred. A groove type or cylindrical drier which employs conduction heating system to stir the polycarbonate resin is preferred, and a groove type drier is particularly preferred. The drying temperature is preferably in the range of 130 to 150°C.

In the present invention, the form of the polycarbonate resin to be kneaded and extruded may be powdery, particulate, flaky or pellet and preferably powdery, particulate or flaky.

In the present invention, the polycarbonate resin to be kneaded and extruded has a chlorine atom content of preferably 5 to 2,000 ppm, more preferably 5 to 1,500 ppm. When the chlorine atom content falls within the above range, the object of the present invention is effectively attained.

<double-screw extruder>

The double-screw extruder has at least one kneading/extrusion unit which comprises (1) a water inlet part, (2) a kneading part, (3) a seal ring and (4) a vent part. Preferably, the double-screw extruder further has (5) an auxiliary vent part and (6) an additive introduction part. Fig. 1 shows an example of the structure of the double-screw extruder used in the present invention.

(water inlet part (1))

The water inlet part is a part for injecting water. When the number of the water inlet parts is 6 or more, the deterioration of the resin occurs disadvantageously.

(kneading part (2))

The kneading part is situated right below the water inlet part in the extruder and a part for kneading the resin. In the present invention, the screw constitution of the kneading part is important.

The screw element at the most upstream of the kneading part is an orthogonal kneading disk (c) or a forward kneading disk (f) and the screw element at the most downstream is a backward kneading disk (r).

As examples of the screw constitution, a combination of the forward kneading disk (f) and the backward kneading disk (r), a combination of the orthogonal kneading disk (c) and the backward kneading disk (r), a combination of kneading disks (c), (f) and (r), a combination of kneading disks (f), (c) and (r), a combination of kneading disks (c), (c), (r) and (r), and a combination of kneading disks (f), (f), (r) and (r) are preferred.

Kneading disks of a double-start thread type are preferred. The helix angle of the kneading disk is

preferably 15 to 90°, more preferably 45 to 90°. Each kneading disk is composed of a plurality of disks and the number of disks is preferably 2 to 7, more preferably 3 to 6.

5 The length (L_1) of each screw element of the kneading part is 0.25D to D, preferably 0.5D to 0.75D. D represents the inner diameter of the cylinder. The length (L_2) of the kneading part is D to 4D, preferably 1.5D to 3.5D. The total length (L_3) of all the screws is preferably 28D to 49D, more
10 preferably 31.5D to 45.5D.

 When the screw of the kneading part is constituted as described above, the content of the chlorine compound in the obtained polycarbonate pellet is reduced. A molded article formed from the obtained pellet has a small amount of a
15 chlorine ion eluted by water and is advantageously used as a storage and transport container for silicon wafers or magnetic disks.

(seal ring (3))

20 The seal ring is located on the upstream side, downstream side or both sides of the kneading part.

(vent part (4))

 The vent part is located on the downstream side of the water inlet part and a part for discharging a gas formed by
25 kneading.

(auxiliary vent part (5))

 The double-screw extruder preferably has an auxiliary
30 vent part on the upstream side of the kneading/extrusion unit. Therefore, the number of vent parts of the double-screw extruder is preferably 2 or more, more preferably 2 to 6, much more preferably 2 to 5. When the number of vents is 1, the content of the residual chlorine ion in the obtained

polycarbonate resin pellet tends to become high and when the number of vents is too large, the total length (L_3) of all the screws of the extruder becomes large, thereby exerting bad influences such as the yellowing of the resin and the deterioration of the resin.

The number of the kneading/extrusion units of the double-screw extruder is preferably 1 to 5, more preferably 1 to 3, much more preferably 1 to 2.

(additive introduction part (6))

The double-screw extruder may have an additive introduction part on the downstream side of the kneading/extrusion unit. The double-screw extruder preferably has an auxiliary kneading part on the downstream side of the additive introduction part. The auxiliary kneading part may be provided in the screw on the downstream side of the additive introduction part to enhance the dispersibility of additives. The screw constitution of the auxiliary kneading part is not particularly limited if the additives can be fully kneaded. For example, a forward kneading disk, orthogonal kneading disk and backward kneading disk may be used alone or in combination.

<kneading condition>

Kneading is carried out by injecting water from the water inlet part and setting the vacuum degree of the vent part to 6.7 kPa or less.

When the amount of water added from the water inlet part is too small, the effect obtained by injecting water is not obtained and the content of the chlorine atom in the obtained polycarbonate resin pellet is not reduced. When the amount is too large, deaeration in the vent part becomes unsatisfactory, which exerts a bad influence such as hydrolysis on the polycarbonate resin. Therefore, the

amount of water injected from the water inlet part is preferably 0.1 to 5 parts by weight, more preferably 0.2 to 4 parts by weight based on 100 parts by weight of the polycarbonate resin.

5 Water to be injected has an electric conductivity measured at 25°C of preferably 1 $\mu\text{S}/\text{cm}$ or less, more preferably 0.5 $\mu\text{S}/\text{cm}$ or less. When water having an electric conductivity of 1 $\mu\text{S}/\text{cm}$ or less is used, the hydrolysis of the polycarbonate resin occurs more rarely and a reduction
10 in the molecular weight of the resin is suppressed advantageously.

 Further, the vacuum degree of each vent of the double-screw extruder is 6.7 kPa or less, preferably 2.0 kPa or less. When the vacuum degree falls within the above range,
15 the injected water is completely removed in the vent part and the amount of the chlorine atom becomes small, thereby not exerting a bad influence such as hydrolysis on the aromatic polycarbonate resin advantageously.

 The method of introducing the additives is not
20 particularly limited and the additives may be introduced independently, or a plurality of additives may be blended and introduced. An additive master prepared by blending additives with a polycarbonate resin powder as a raw material may be added. When the additives have a low melting point,
25 they may be molten and block in the additive introduction part. Therefore, it is preferred that the additive master prepared by blending the additives with the polycarbonate resin powder should be introduced into the double-screw extruder.

30 As for the total amount of the introduced additives which depends on the required properties, when the additive master is introduced, the amount of the additive master is preferably 0.1 to 30 wt% based on the obtained polycarbonate resin pellet (total amount of extrusion). It is more

preferably 0.2 to 20 wt%, much more preferably 0.3 to 10 wt%. When the additive master is introduced in an amount above this range, the effect of reducing the amount of the chlorine compound tends to become unsatisfactory and when the additive master is introduced in an amount below the above range, variations in the total amount of the introduced additives become large and the required properties may not be provided.

Therefore, the additive master prepared by blending the additives with the polycarbonate resin powder is preferably introduced into the double-screw extruder from the additive introduction part in an amount of 0.1 to 30 wt% based on the obtained pellet.

<additives>

Various additives may be contained in the polycarbonate resin pellet of the present invention and a molded article formed from the pellet in limits not prejudicial to the object of the present invention in order to provide various properties. The additives include a release agent, heat stabilizer, ultraviolet absorbent, bluing agent, antistatic agent, flame retardant, heat ray blocking agent, fluorescent dye (including fluorescent brightening agent), pigment, light diffusing agent, reinforcement, other resin and elastomer.

Preferably, the release agent comprises 90 wt% or more of an ester of an alcohol and a fatty acid. The ester of an alcohol and a fatty acid is, for example, an ester of a monohydric alcohol and a fatty acid and/or a partial or whole ester of a polyhydric alcohol and a fatty acid. The ester of a monohydric alcohol and a fatty acid is preferably an ester of a monohydric alcohol having 1 to 20 carbon atoms and a saturated fatty acid having 10 to 30 carbon atoms. The partial or whole ester of a polyhydric alcohol and a fatty acid is preferably a partial or whole ester of a polyhydric

alcohol having 1 to 25 carbon atoms and a saturated fatty acid having 10 to 30 carbon atoms.

Examples of the ester of a monohydric alcohol and a saturated fatty acid include stearyl stearate, palmityl
5 palmitate, butyl stearate, methyl laurate and isopropyl palmitate, out of which stearyl stearate is preferred.

Examples of the partial or whole ester of a polyhydric alcohol and a saturated fatty acid include monoglyceride stearate, diglyceride stearate, triglyceride stearate,
10 monosorbitate stearate, monoglyceride behenate, pentaerythritol monostearate, pentaerythritol tetrastearate, pentaerythritol tetrapelargonate, propylene glycol monostearate, biphenyl biphenate, sorbitan monostearate, 2-ethylhexyl stearate and a partial or whole
15 ester of a dipentaerythritol such as dipentaerythritol hexastearate.

Out of these esters, monoglyceride stearate, triglyceride stearate, pentaerythritol tetrastearate and a mixture of triglyceride stearate and stearyl stearate are
20 preferred.

The content of the above ester in the release agent is 90 wt% or more, more preferably 95 wt% or more based on 100 wt% of the release agent.

The content of the release agent in the polycarbonate resin powder is 0.005 to 2.0 parts by weight, more preferably
25 0.01 to 0.6 part by weight, much more preferably 0.02 to 0.5 part by weight based on 100 parts by weight of the polycarbonate resin powder.

The heat stabilizer is selected from a
30 phosphorus-based heat stabilizer, sulfur-based heat stabilizer and hindered phenol-based heat stabilizer.

The phosphorus-based heat stabilizer is a phosphorous acid, phosphoric acid, phosphonous acid, phosphonic acid or ester thereof, as exemplified by triphenyl phosphite,

tris(nonylphenyl)phosphite,
 tris(2,4-di-tert-butylphenyl)phosphite,
 tris(2,6-di-tert-butylphenyl)phosphite, tridecyl
 phosphite, trioctyl phosphite, trioctadecyl phosphite,
 5 didecylmonophenyl phosphite, dioctylmonophenyl phosphite,
 diisopropylmonophenyl phosphite, monobutyldiphenyl
 phosphite, monodecyldiphenyl phosphite, monooctyldiphenyl
 phosphite,
 bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol
 10 diphosphite,
 2,2-methylenebis(4,6-di-tert-butylphenyl)octyl phosphite,
 bis(nonylphenyl)pentaerithritol diphosphite,
 bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite,
 distearyl pentaerythritol diphosphite, tributyl phosphate,
 15 triethyl phosphate, trimethyl phosphate, triphenyl
 phosphate, diphenylmonoorthoxenyl phosphate, dibutyl
 phosphate, dioctyl phosphate, diisopropyl phosphate,
 dimethyl benzenephosphonate, diethyl benzenephosphonate,
 dipropyl benzenephosphonate,
 20 tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene
 diphosponite,
 tetrakis(2,4-di-tert-butylphenyl)-4,3'-biphenylene
 diphosponite,
 tetrakis(2,4-di-tert-butylphenyl)-3,3'-biphenylene
 25 diphosponite,
 bis(2,4-di-tert-butylphenyl)-4-phenyl-phenyl phosphonite
 and bis(2,4-di-tert-butylphenyl)-3-phenyl-phenyl
 phosphonite.

Out of these, tris(2,4-di-tert-butylphenyl)phosphite,
 30 tris(2,6-di-tert-butylphenyl)phosphite,
 tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene
 diphosponite,
 tetrakis(2,4-di-tert-butylphenyl)-4,3'-biphenylene
 diphosponite,

tetrakis(2,4-di-tert-butylphenyl)-3,3'-biphenylene
diphosphonite,
bis(2,4-di-tert-butylphenyl)-4-phenyl-phenyl phosphonite
and bis(2,4-di-tert-butylphenyl)-3-phenyl-phenyl
5 phosphonite are preferred, and
tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene
diphosphonite is particularly preferred.

The content of the phosphorus-based heat stabilizer
in the polycarbonate resin powder is preferably 0.001 to 0.2
10 part by weight based on 100 parts by weight of the
polycarbonate resin powder.

Examples of the sulfur-based heat stabilizer include
pentaerythritol-tetrakis(3-laurylthiopropionate),
pentaerythritol-tetrakis(3-myristylthiopropionate),
15 pentaerythritol-tetrakis(3-stearylthiopropionate),
dilauryl-3,3'-thiodipropionate,
dimyristyl-3,3'-thiodipropionate and
distearyl-3,3'-thiodipropionate, out of which
pentaerythritol-tetrakis(3-laurylthiopropionate),
20 pentaerythritol-tetrakis(3-myristylthiopropionate),
dilauryl-3,3'-thiodipropionate and
dimyristyl-3,3'-thiodipropionate are preferred.
Pentaerythritol-tetrakis(3-laurylthiopropionate) is
particularly preferred. This thioether-based compound is
25 commercially available from Sumitomo Chemical Co., Ltd.
under the trade names of Sumilizer TP-D and Sumilizer TPM
and can be easily used.

The content of the sulfur-based heat stabilizer in the
polycarbonate resin powder is preferably 0.001 to 0.2 part
30 by weight based on 100 parts by weight of the polycarbonate
resin powder.

Examples of the hindered phenol-based heat stabilizer
include triethylene
glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)]

propionate],
 1,6-hexanediol-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)
 propionate],
 pentaerythritol-tetrakis[3-(3,5-di-tert-butyl-4-
 5 hydroxyphenyl)propionate],
 octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)
 propionate,
 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-
 hydroxybenzyl)benzene,
 10 N,N-hexamethylenebis(3,5-di-tert-butyl-4-hydroxy-
 hydrocinnamide),
 3,5-di-tert-butyl-4-hydroxy-benzylphosphonate-
 diethyl ester,
 tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate and
 15 3,9-bis{1,1-dimethyl-2-[β -(3-tert-butyl-4-hydroxy-5-
 methylphenyl)propionyloxy]ethyl}-2,4,8,10-tetraoxaspiro
 (5,5)undecane, out of which
 octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)
 propionate is particularly preferred.

20 The content of the hindered phenol-based heat
 stabilizer in the polycarbonate resin powder is preferably
 0.001 to 0.3 part by weight based on 100 parts by weight of
 the polycarbonate resin powder.

The ultraviolet light absorber is preferably at least
 25 one selected from the group consisting of a
 benzotriazole-based ultraviolet absorber,
 benzophenone-based ultraviolet absorber, triazine-based
 ultraviolet absorber, cyclic iminoester-based ultraviolet
 absorber and cyanoacrylate-based ultraviolet absorber.

30 Examples of the benzotriazole-based ultraviolet
 absorber include

2-(2-hydroxy-5-methylphenyl)benzotriazole,
 2-(2-hydroxy-5-tert-octylphenyl)benzotriazole,
 2-(2-hydroxy-3,5-dicumylphenyl)phenylbenzotriazole,

2- (2-hydroxy-3-tert-butyl-5-methylphenyl) -5-chlorobenzotriazole,
 2,2'-methylenebis[4- (1,1,3,3-tetramethylbutyl) -6- (2N-benzotriazol-2-yl)phenol],
 5 2- (2-hydroxy-3,5-di-tert-butylphenyl)benzotriazole,
 2- (2-hydroxy-3,5-di-tert-butylphenyl) -5-chlorobenzotriazole, 2- (2-hydroxy-3,5-di-tert-amylphenyl)benzotriazole,
 2- (2-hydroxy-5-tert-octylphenyl)benzotriazole,
 10 2- (2-hydroxy-5-tert-butylphenyl)benzotriazole,
 2- (2-hydroxy-4-octoxyphenyl)benzotriazole,
 2,2'-methylenebis(4-cumyl-6-benzotriazolephenyl),
 2,2'-p-phenylenebis(1,3-benzoxazin-4-one) and
 2- [2-hydroxy-3- (3,4,5,6-tetrahydrophthalimidomethyl) -5-methylphenyl]benzotriazole. They may be used alone or in
 15 combination of two or more.

2- (2-hydroxy-5-methylphenyl)benzotriazole,
 2- (2-hydroxy-5-tert-octylphenyl)benzotriazole,
 2- (2-hydroxy-3,5-dicumylphenyl)phenylbenzotriazole,
 20 2- (2-hydroxy-3-tert-butyl-5-methylphenyl) -5-chlorobenzotriazole,
 2,2'-methylenebis[4- (1,1,3,3-tetramethylbutyl) -6- (2H-benzotriazol-2-yl)phenol] and
 2- [2-hydroxy-3- (3,4,5,6-tetrahydrophthalimidomethyl) -5-methylphenyl]benzotriazole are preferred, and
 25 2- (2-hydroxy-5-tert-octylphenyl)benzotriazole and
 2,2'-methylenebis[4- (1,1,3,3-tetramethylbutyl) -6- (2H-benzotriazol-2-yl)phenol] are more preferred.

Examples of the benzophenone-based ultraviolet
 30 absorber include 2,4-dihydroxybenzophenone,
 2-hydroxy-4-methoxybenzophenone,
 2-hydroxy-4-octoxybenzophenone,
 2-hydroxy-4-benzyloxybenzophenone,
 2-hydroxy-4-methoxy-5-sulfoxybenzophenone,

2-hydroxy-4-methoxy-5-sulfoxytrihydriderate benzophenone,
 2,2'-dihydroxy-4-methoxybenzophenone,
 2,2',4,4'-tetrahydroxybenzophenone,
 2,2'-dihydroxy-4,4'-dimethoxybenzophenone,
 5 2,2'-dihydroxy-4,4'-dimethoxy-5-sodiumsulfoxy
 benzophenone,
 bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methane,
 2-hydroxy-4-n-dodecyloxybenzophenone and
 2-hydroxy-4-methoxy-2'-carboxybenzophenone.

10 Examples of the triazine-based ultraviolet absorber
 include

2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-
 phenol, and
 2-(4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl)-5-
 15 [(octyl)oxy]-phenol.

Examples of the cyclic iminoester-based ultraviolet
 absorber include 2,2'-bis(3,1-benzoxazin-4-one),
 2,2'-p-phenylenebis(3,1-benzoxazin-4-one),
 2,2'-m-phenylenebis(3,1-benzoxazin-4-one),
 20 2,2'-(4,4'-diphenylene)bis(3,1-benzoxazin-4-one),
 2,2'-(2,6-naphthalene)bis(3,1-benzoxazin-4-one),
 2,2'-(1,5-naphthalene)bis(3,1-benzoxazin-4-one),
 2,2'-(2-methyl-p-phenylene)bis(3,1-benzoxazin-4-one),
 2,2'-(2-nitro-p-phenylene)bis(3,1-benzoxazin-4-one) and
 25 2,2'-(2-chloro-p-phenylene)bis(3,1-benzoxazin-4-one).

Out of these, 2,2'-p-phenylenebis(3,1-benzoxazin-4-one),
 2,2'-(4,4'-diphenylene)bis(3,1-benzoxazin-4-one) and
 2,2'-(2,6-naphthalene)bis(3,1-benzoxazin-4-one) are
 preferred, and 2,2'-p-phenylenebis(3,1-benzoxazin-4-one)
 30 is particularly preferred. This compound is commercially
 available from Takemoto Oil & Fat Co., Ltd. under the trade
 name of CEi-P and can be easily used.

Examples of the cyanoacrylate-based ultraviolet
 absorber include

1,3-bis-[(2'-cyano-3',3'-diphenylacryloyl)oxy]-2,2-bis[(2-cyano-3,3-diphenylacryloyl)oxy]methyl)propane and 1,3-bis-[(2-cyano-3,3-diphenylacryloyl)oxy]benzene.

The amount of the ultraviolet absorber is preferably
5 0.01 to 3.0 parts by weight, more preferably 0.02 to 1.0 part by weight, much more preferably 0.05 to 0.8 part by weight based on 100 parts by weight of the polycarbonate resin powder. Within the above range, sufficiently high weatherability can be provided to a polycarbonate resin molded article according
10 to application purpose.

Examples of the bluing agent include the Macrolex Violet B and Macrolex Blue RR of Bayer AG. and the Polysynthrene Blue RLS of Clariant International Ltd. The bluing agent is effective in erasing the yellow tinge of the
15 polycarbonate resin powder. Since a polycarbonate resin powder provided with weatherability contains a predetermined amount of an ultraviolet absorber, a molded article of the polycarbonate resin is apt to be tinged with yellow according to "the function and color of the ultraviolet absorber". To
20 provide natural transparency to a sheet or lens in particular, use of the bluing agent is very effective.

The amount of the bluing agent is preferably 0.05 to 1.5 ppm, more preferably 0.1 to 1.2 ppm based on the polycarbonate resin powder.

25 The resin temperature for kneading and extruding the polycarbonate resin which is suitably set according to the molecular weight of the polycarbonate resin or the like is preferably about 270 to 350°C.

30 <molded article>

The polycarbonate resin pellet obtained by the above process is molded by a commonly used method such as extrusion molding or injection molding. The present invention includes a molded article formed from the polycarbonate resin

pellet obtained by the above process.

In the molded article formed from the polycarbonate resin pellet, the amount of the chlorine ion which is eluted by water is greatly reduced.

5 The amount of the chlorine ion eluted into water from the molded article when it is heated at 80°C for 24 hours in water is preferably 10 ng/cm² or less, more preferably 9 ng/cm² or less. Although the lower limit is not particularly limited, it is difficult to set it to 0.5 ng/cm²
10 or less. The molded article is advantageously used as a storage and transport container for silicon wafers or magnetic disks.

Examples

15 The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting. "Parts" in the examples means parts by weight and "%" means wt% unless stated otherwise. The examples were evaluated by the following methods.

20 (1) Amount of chlorine ion

A sample board having a thickness of 1 mm obtained by injection molding the polycarbonate resin pellet was cut to a length of 20 mm and a width of 25 mm, the obtained sample was put into an extraction pack, 15 cm³ of super pure water
25 was injected into the pack, and the pack was sealed up and heated at 80°C for 24 hours. Then, it was cooled to room temperature, and the amount of Cl⁻ contained in water was determined by ion chromatography to obtain the amount of the extracted Cl⁻ based on 1 cm³ of the surface area of the molded
30 article. The used apparatus and conditions are shown in Table 1 below.

Table 1

Apparatus	DX-500 of DIONEX CORPORATION
Amount of injected sample	0.5cm ³
Eluant	NaOH
Separation column	IonPac AS4A-SC
Detector	Electric conductivity meter

(2) Content of chlorine atom

The polycarbonate resin pellet was completely burnt
 5 and the generated hydrogen chloride (HCl) was potentially
 titrated with a silver ion (Ag⁺) to obtain the content of
 the chlorine atom from the amount of electricity required
 for this potential titration.

10 (3) Hue (b value of pellet):

The b value was measured with a hue meter (SE-2000 of
 Nippon Denshoku Industries Co. Ltd.). As the b value becomes
 larger, the pellet is more tinged with yellow, which means
 that the polycarbonate resin deteriorated in heat stability
 15 at the time of melt extrusion.

Examples 1 to 11 and Comparative Examples 1 to 5

A raw material resin and additives shown in Table 2
 were supplied into a double-screw extruder [TEX30α of The
 20 Japan Steel Works, Ltd., L₃/D of entire screw constitution
 = 45.5] having 3 vents (V1, V2 and V3 from the raw material
 feed hopper) and water inlet parts right before vents V2 and
 V3 (W1 and W2 from the raw material feed hopper) and a screw
 diameter of 30 mm shown in Figs. 2 to 7, and the obtained
 25 product was extruded into a strand under extrusion conditions
 shown in Table 2 and cut to produce a pellet.

A master powder having a concentration 50 times higher
 than the target total amount of added substances was prepared

by blending the additives with the following resin raw material C and introduced from the additive introduction part in an amount of 2 wt% based on the obtained polycarbonate resin pellet (total amount of the resin raw material and the master powder). The target amounts of the additives are shown in Table 3. The evaluation results of the obtained polycarbonate resin pellets are shown in Table 4.

The Letters for the raw material resins, the additives and the screw of the water inlet part in Table 2 denote the following.

Resin raw material A: polycarbonate resin powder having a viscosity average molecular weight of 18,500 obtained by reacting bisphenol A with phosgene in methylene chloride in accordance with a commonly used method (amount of chlorine atom: 50 ppm)

Resin raw material B: polycarbonate resin powder having a viscosity average molecular weight of 18,500 obtained by reacting bisphenol A with phosgene in methylene chloride in accordance with a commonly used method (amount of chlorine atom: 236 ppm)

Resin raw material C: polycarbonate resin powder having a viscosity average molecular weight of 22,400 obtained by reacting bisphenol A with phosgene in methylene chloride in accordance with a commonly used method (amount of chlorine atom: 88 ppm)

Additives:

Ultraviolet absorber;

2-(2-hydroxy-5-tert-octylphenyl)benzotriazole

Release agent: pentaerythritol tetrastearate

Phosphorus-based stabilizer;

tris(2,4-di-tert-butylphenyl)phosphite

Hindered phenol-based heat stabilizer;

octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate

Bluing agent; Microlex Violet B of Bayer AG.

Screw A (see Fig. 2):

Having such screw constitution in the water inlet part (helix angle of the screw element of the kneading part is 90° for the orthogonal kneading disk and 45° for the backward kneading disk, L_2 is 2.0D) that a seal ring (length of 0.5D) is arranged at a position 1.0D on the upstream side from the nozzle of the water inlet part of the extruder, and two orthogonal kneading disks (length of 0.5D; each consisting of 5 disks having a length of 0.1D), two backward kneading disks (length of 0.5D; each consisting of 5 disks having a length of 0.1D) and a seal ring (length of 0.5D) are arranged from the ring toward the downstream side.

Screw B (see Fig. 3):

Having such screw constitution in the water inlet part (helix angle of the screw element of the kneading part is 45° for the forward kneading disk and 45° for the backward kneading disk, L_2 is 2.0D) that a seal ring (length of 0.5D) is arranged at a position 1.0D on the upstream side from the nozzle of the water inlet part of the extruder, and three forward kneading disks (length of 0.5D; each consisting of 5 disks having a length of 0.1D), one backward kneading disk (length of 0.5D; consisting of 5 disks having a length of 0.1D) and a seal ring (length of 0.5D) are arranged from the ring toward the downstream side.

Screw C (see Fig. 4):

Having such screw constitution that the seal ring (length of 0.5D) arranged at a position 1.0D on the upstream side from the nozzle of the water inlet part of the extruder in the screw A is replaced by an ordinary full flight disk
Screw D (see Fig. 5):

Having such screw constitution (helix angle of the screw element of the auxiliary kneading part is 45° for the forward kneading disk, L_2 is 1.0D) that an additive

introduction part is provided on the downstream side of the vent (V3) on the downstream side of the water inlet part (W2) of the extruder and two forward kneading disks (length of $0.5D$; each consisting of 5 disks having a length of $0.1D$) are arranged on the downstream side of the additive introduction part in the screw A.

Screw E (see Fig. 6):

Having such screw constitution that a forward kneading disk is used in place of the backward kneading disk in the screw B

Screw F (see Fig. 7):

Having such screw constitution that a forward kneading disk is used in place of the orthogonal kneading disk and the backward kneading disk in the screw D

Table 2

Examples	Type of resin raw material	Additives	Screw constitution	Amount of extrusion (kg/hr)	Revolution of screw (rpm)	Amount of injected water (wt%)			Vacuum degree of vent (kpa)		
						W1	W2		V1	V2	V3
Ex. 1	A	Not introduced	A	30	251	0.52	0.53		1.30	1.28	1.31
Ex. 2	A	Not introduced	A	30	251	0.54	—		1.27	1.30	—
Ex. 3	A	Not introduced	B	30	251	0.54	0.52		1.28	1.30	1.31
Ex. 4	A	Not introduced	B	30	251	0.51	—		1.31	1.29	—
Ex. 5	B	Not introduced	A	30	251	0.50	0.50		1.30	1.33	1.33
Ex. 6	B	Not introduced	A	30	250	0.52	—		1.27	1.28	—
Ex. 7	B	Not introduced	B	30	250	0.51	—		1.31	1.33	—
Ex. 8	A	Not introduced	C	30	251	0.52	—		1.30	1.30	—
Ex. 9	A	Not introduced	C	30	251	0.52	0.50		1.29	1.30	1.29
Ex. 10	C	Introduced	D	30	251	0.51	—		1.30	1.31	1.33
Ex. 11	C	Introduced	D	30	251	0.51	—		1.30	1.30	—
C.Ex. 1	A	Not introduced	B	30	252	0.52	—		7.20	7.20	—
C.Ex. 2	B	Not introduced	B	30	249	0.55	—		7.20	7.20	—
C.Ex. 3	C	Introduced	D	30	251	0.50	—		7.20	7.20	—
C.Ex. 4	A	Not introduced	E	30	251	0.54	—		1.30	1.30	—
C.Ex. 5	C	Introduced	F	30	250	0.51	—		1.30	1.30	—

Ex.: Example C.Ex.: Comparative Example

Table 3

Additives	Amount
Ultraviolet absorber	0.2wt%
Release agent	0.1wt%
Phosphorus-based stabilizer	0.03wt%
Hindered phenol-based stabilizer	0.05wt%
Bluing agent	0.5ppm

Table 4

Example	Amount of eluted chlorine ion (ng/cm ²)	content of chlorine atom in pellet (ppm)	b value of pellet
Example 1	4	1	-0.2
Example 2	7	1	0.0
Example 3	6	1	-0.1
Example 4	9	1	0.1
Example 5	4	1	-0.2
Example 6	8	1	0.0
Example 7	9	1	0.1
Example 8	4	1	0.0
Example 9	8	1	0.0
Example 10	6	1	-2.3
Example 11	9	1	-2.5
Comparative Example 1	11	2	0.3
Comparative Example 2	11	2	0.4
Comparative Example 3	12	3	-2.5
Comparative Example 4	13	3	0.1
Comparative Example 5	14	3	-2.5

Example 12 and Comparative Example 6

A storage and transport container for silicon wafers was molded from each of the pellets obtained in Example 1 and Comparative Example 1. This storage and transport
5 container for silicon wafers was immersed in 80°C hot water for 24 hours. Thereafter, the container was dried, a predetermined number of silicon wafers were inserted into this container, kept at normal temperature in the closed container for 1 week and taken out from the container, and
10 the contact angle between water and the surface of the wafer was measured at 5 positions of the surface. The average of the measured contact angles is shown in Table 5. The contact angle between water and the surface of the wafer is a measure of the degree of the surface contamination of the wafer. When
15 the contact angle is large, the hydrophobic nature of the surface of the wafer is high and the degree of contamination is high. The contact angle is preferably 10° or less.

Table 5

	Contact angle	
	Before insertion	After keeping
Example 12	3.5	3.8
Comparative Example 6	3.5	12.5

20

Effect of the Invention

According to the present invention, a polycarbonate resin having a low content of a chlorine atom and a small amount of an eluted chlorine ion is obtained by using a vented
25 double-screw extruder having a material seal and a screw with an excellent water dispersion effect in the kneading part of the wafer inlet part. According to the present invention, a polycarbonate resin which is preferred as a material for a storage and transport container which rarely contaminates

the surface of its content is obtained. According to the present invention, a polycarbonate resin which is preferred as a material for a storage and transport container for silicon wafers or magnetic disks is obtained. According to
5 the present invention, a storage and transport container which rarely contaminates the surface of its content is obtained.

Industrial Applicability

10 The polycarbonate resin obtained by the manufacturing process of the present invention is advantageously used as a material for forming a storage and transport container for silicon wafers or magnetic disks which are sensitive to surface contamination.

CLAIMS

1. A process of manufacturing a pellet for a storage and transport container for silicon wafers or magnetic disks by melt extruding a polycarbonate resin powder from a double-screw extruder, wherein

(i) the double-screw extruder has at least one kneading/extrusion unit which comprises a water inlet part, a kneading part right below the water inlet part, a seal ring located on both the upstream side, and downstream side of the kneading part and a vent part on the downstream side of the water inlet part;

(ii) a screw element at the most upstream of the kneading part is an orthogonal kneading disk (c) or a forward kneading disk (f) and a screw element at the most downstream is a backward kneading disk (r);

(iii) the length (L_1) of each screw element of the kneading part is $0.25D$ to D , and the length (L_2) of the kneading part is D to $4D$ (D is the inner diameter of a cylinder); and

water is injected from the water inlet part (W) and the vacuum degree of the vent part (V) is set to 6.7 kPa or less.

2. The manufacturing process according to claim 1, wherein the double-screw extruder has an additive introduction part on the downstream side of the kneading/extrusion unit, and an additive is introduced therefrom.

3. The manufacturing process according to claim 2, wherein the double-screw extruder has an auxiliary kneading part on the downstream side of the additive introduction part.

4. The manufacturing process according to claim 2, wherein an additive master prepared by blending additive with the polycarbonate resin powder is introduced into the double-screw extruder from the additive introduction part in an amount of 0.1 to 30 wt% based on the obtained pellet.
5. The manufacturing process according to claim 1, wherein the double-screw extruder has a total length (L_3) of all the screws of 28D to 49D (D is the inner diameter of the cylinder).
6. The manufacturing process according to claim 1, wherein the double-screw extruder has an auxiliary vent part on the upstream side of the kneading/extrusion unit.
7. The manufacturing process according to claim 1, wherein the amount of injected water is 0.1 to 5 parts by weight based on 100 parts by weight of the polycarbonate resin.
8. A storage and transport container for silicon wafers or magnetic disks formed from the polycarbonate resin pellet obtained by the manufacturing process of claim 1.
9. The storage and transport container according to claim 8, wherein the amount of a chlorine ion eluted into water from the container after it is heated at 80°C for 24 hours in water is 10 ng/cm² or less.

Abstract

The present invention provides a process of manufacturing a polycarbonate resin having a low content of a chlorine atom and a small amount of an eluted chlorine ion by melt extruding a polycarbonate resin powder from a double-screw extruder to produce a pellet, wherein

(i) the double-screw extruder has at least one kneading/extrusion unit which comprises a water inlet part, a kneading part, a seal ring and a vent part;

(ii) a screw element at the most upstream of the kneading part is an orthogonal kneading disk (c) or a forward kneading disk (f) and a screw element at the most downstream is a backward kneading disk (r);

(iii) the length of each screw element of the kneading part is $0.25D$ to D , and the length of the kneading part is D to $4D$; and

water is injected from the water inlet part and the vacuum degree of the vent part is set to 6.7 kPa or less.