

DESCRIPTION

CARBONYL CHLORIDE PRODUCTION PROCESS

5 TECHNICAL FIELD

The present invention relates to a carbonyl chloride production process. The present invention also relates to a process for producing a polycarbonate resin from the obtained carbonyl chloride.

10

BACKGROUND ART

Polycarbonate resin has excellent optical properties, mechanical properties and electric properties and therefore has been used in a wide variety of fields including food
15 products, optical products such as multi-media recording media, housings for silicon wafers and multi-media recording media, electric appliances and automobiles.

The polycarbonate resin is generally produced from carbonyl chloride, and it is well known that a by-product
20 and impurities contained in this carbonyl chloride have an influence upon the quality of the polycarbonate resin.

For example, Patent Document 1 discloses a process for producing a polycarbonate resin having a good color from carbonyl chloride which is produced from carbon monoxide
25 having a reduced content of a sulfur compound.

Carbon tetrachloride is a by-product formed at the time of producing carbonyl chloride. It is known that about 150 to 300 ppm of carbon tetrachloride is generally formed at the time of producing carbonyl chloride and contained in the
30 formed carbonyl chloride. It is also known that carbon tetrachloride deteriorates the color of the obtained polycarbonate resin and reduces the mold corrosion resistance, and it is therefore necessary to reduce the content of carbon tetrachloride in the polycarbonate resin

as much as possible.

Some methods for solving these problems have been proposed. For example, Patent Document 2 discloses a process for producing a polycarbonate resin which rarely corrodes
5 a metal mold by using carbonyl chloride whose carbon tetrachloride content has been reduced by distillation.

Patent Document 3 discloses a process for obtaining a polycarbonate resin having improved quality from carbonyl chloride whose sulfur compound and carbon tetrachloride
10 contents have been reduced by the distillation of liquefied carbonyl chloride obtained by dividing a reaction for obtaining carbonyl chloride among many reactors to remove reaction heat as much as possible.

Patent Document 4 discloses a process for obtaining
15 a polycarbonate resin having improved quality from carbonyl chloride whose carbon tetrachloride and volatile chlorine contents have been reduced by the distillation of liquefied carbonyl chloride obtained by dividing a reaction for obtaining carbonyl chloride among many reactors to remove
20 reaction heat as much as possible.

However, to carry out these processes, the process becomes large in scale and complicated and a gas pressure loss becomes large, which is not preferred from the viewpoint of cost.

25 Patent Document 5 discloses a process for obtaining a polycarbonate resin having a low content of chlorine (volatile chlorine) which is evaporated from a molded article after melt molding at normal temperature by using carbonyl chloride having a chlorine content of 1,000 ppb or less which
30 is produced by letting liquefied carbonyl chloride pass through an activated carbon tower to adsorb chlorine contained in carbonyl chloride to the activated carbon.

Meanwhile, some processes for producing carbonyl chloride whose total content of impurities such as carbon

tetrachloride has been reduced are proposed. For example, Patent Document 6 discloses a process for producing carbonyl chloride having a low carbon tetrachloride content and a low chlorine molecule content by using activated carbon having a specific surface area of 1,200 to 1,300 m²/g. However, in the proposal of this Patent Document 6, the reduction of the carbon tetrachloride content is not satisfactory and further, Patent Document 7 is aimed to reduce the content of carbon tetrachloride by distilling carbonyl chloride obtained by the process disclosed by Patent Document 6.

Patent Document 8 discloses a process for producing carbonyl chloride having a reduced content of carbon tetrachloride by using activated carbon having a low active metal content. It teaches that activated carbon having a surface area of more than 100 m²/g is used, specifically 350 to 500 m²/g.

Patent Document 9 discloses a process for producing carbonyl chloride whose carbon tetrachloride content has been reduced by using activated carbon having a surface area of at least 10 m²/g. Actually, activated carbon having a surface area of about 600 to 1,700 m²/g is used.

Patent Document 10 discloses a process for producing carbonyl chloride while the amount of by-produced CCl₄ is reduced by contact with a first catalyst and then with a second catalyst having higher relative activity than the first catalyst in a carbonyl chloride forming reaction.

In all of the proposals of the above patent documents, the improvement of the quality of carbonyl chloride is described from the short-term point of view. However, a process for producing high-quality carbonyl chloride continuously for a long time on an industrial scale is not disclosed by any of these patent documents. To produce carbonyl chloride on an industrial scale, the quality and production cost of the obtained carbonyl chloride are

important but much attention must be paid to safety because carbonyl chloride is a highly toxic substance. Since a disaster risk caused by the leakage of carbonyl chloride becomes large particularly when a catalyst is replaced due to the end of the life of the catalyst, it is desired that the life of the catalyst should be extended as long as possible to reduce the frequency of replacement.

- (Patent Document 1) JP-A 01-275630
(Patent Document 2) JP-B 06-076482
10 (Patent Document 3) JP-A 2000-248059
(Patent Document 4) JP-A 2000-154244
(Patent Document 5) JP-A 10-226724
(Patent Document 6) JP-A 2000-264617
(Patent Document 7) JP-A 2001-261321
15 (Patent Document 8) JP-A 2000-505035
(Patent Document 9) JP-A 2002-511045
(Patent Document 10) US Patent Laid-Open Publication
No. 2002/0188156-A

20 DISCLOSURE OF THE INVENTION

It is an object of the present invention to provide a process for producing carbonyl chloride having a low total content of impurities and a good color. It is another object of the present invention to provide a process for producing carbonyl chloride, wherein the deterioration of a catalyst is suppressed and long-term continuous operation is possible.

It is still another object of the present invention to provide a polycarbonate resin having a low content of a metal corrosive substance, a good color and high molding heat stability.

The inventors of the present invention have conducted intensive studies to attain the above objects and have found that not only carbon tetrachloride and a chlorine molecule

contained in carbonyl chloride but also a bromine molecule exert a bad influence upon the color of carbonyl chloride and the color and metal corrosion resistance of a polycarbonate resin obtained from carbonyl chloride.

5 They have conducted further intensive studies and have found that carbonyl chloride having low contents of carbon tetrachloride, a chlorine molecule and a bromine molecule can be produced by using two different catalysts which differ from each other in specific surface area.

10 They have conducted still further intensive studies and have found a process for producing carbonyl chloride, wherein long-term continuous operation is made possible by optimizing the use ratio and particle size distributions of the two different catalysts. The present invention has been
15 accomplished based on these findings.

That is, according to the present invention, the following inventions are provided.

1. A process for producing carbonyl chloride, comprising the steps of:

20 (i) bringing chlorine and carbon monoxide into contact with a first catalyst having a specific surface area of 200 to 800 m²/g; and

 (ii) bringing the obtained product into contact with a second catalyst having a specific surface area of 800 to
25 1,500 m²/g.

2. The production process in the above paragraph 1, wherein the filled volume ratio of the first catalyst to the second catalyst is 4/6 to 9/1.

3. The production process in the above paragraph 1,
30 wherein the first catalyst and the second catalyst are both activated carbon.

4. The production process in the above paragraph 1, wherein the average particle diameters of the first catalyst and the second catalyst are each 0.5 to 5.0 mm.

5. The production process in the above paragraph 1, wherein the average particle diameters of the first catalyst and the second catalyst are each 1.0 to 4.0 mm.
6. The production process in the above paragraph 1, wherein the above contact is carried out at a pressure of 0.05 to 0.50 MPa (gauge pressure).
7. The production process in the above paragraph 1, wherein the obtained carbonyl chloride has a carbon tetrachloride content of 20 ppm or less, a chlorine molecule content of 20 ppm or less and a bromine molecule content of 10 ppm or less when the cumulative production of carbonyl chloride based on 1 m³ of the catalyst is 2.0 x 10⁶ kg/m³ and 1.6 x 10⁷ kg/m³.
8. The production process in the above paragraph 1, wherein the obtained carbonyl chloride has a carbon tetrachloride content of 10 ppm or less, a chlorine molecule content of 10 ppm or less and a bromine molecule content of 5 ppm or less when the cumulative production of carbonyl chloride based on 1 m³ of the catalyst is 2.0 x 10⁶ kg/m³ and 1.6 x 10⁷ kg/m³.
9. Carbonyl chloride having a carbon tetrachloride content of 20 ppm or less, a chlorine molecule content of 20 ppm or less and a bromine molecule content of 10 ppm or less.
10. A process for producing a polycarbonate resin by reacting a dihydric phenol with the carbonyl chloride of the above paragraph 9.
11. A polycarbonate resin having a carbon tetrachloride content of 2 ppm or less, a chlorine atom content of 1 ppm or less and a bromine atom content of 0.5 ppm or less.
12. A molded article obtained by melt molding the polycarbonate resin of the above paragraph 11.

In this text, the chlorine molecule is a molecule formed by bonding two chlorine atoms and generally existent as a

gas in carbonyl chloride.

The chlorine atom content of the polycarbonate resin is the total content of components corresponding to a chlorine atom out of the components of molecules containing a chlorine atom, such as a chlorine molecule, a chlorine bromide molecule and a carbonyl chloride molecule.

In this text, the bromine molecule is a molecule formed by bonding two bromine atoms and generally existent as a gas in carbonyl chloride.

The bromine atom content of the polycarbonate resin is the total content of components corresponding to a bromine atom out of the components of molecules containing a bromine atom, such as a bromine molecule, a chlorine bromide molecule and a carbonyl bromide molecule.

15

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a molded transparent head lamp lens for automobiles molded in Example. As shown in the figures, the lens is shaped like a dome. Fig. [1-A] is a front view of the head lamp lens (projection view on the surface of a platen at the time of molding. Therefore, this area is the maximum projection area) and Fig. [1-B] is a sectional view cut on line A-A.

Explanation of reference numerals

1. head lamp lens body
2. dome-like portion of lens (projection side corresponds to a movable mold)
3. peripheral portion of lens
4. gate of molded article (width of 30 mm, thickness of gate portion of 4 mm)
5. sprue (diameter of gate portion of 7 mm)
6. diameter of peripheral portion of lens (220 mm)
7. diameter of dome portion of lens (200 mm)
8. height of dome portion of lens (20 mm)

9. thickness of molded lens (4 mm)

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in more detail
5 hereinunder.

<carbonyl chloride production process>

The carbonyl chloride production process of the present invention comprises the step of bringing chlorine (may be referred to as "Cl₂" hereinafter) and carbon monoxide
10 (to be referred to as "CO" hereinafter) into contact with a first catalyst in a first reactor and with a second catalyst in a second reactor to react them together.
(chlorine)

The bromine atom content of chlorine used in the
15 reaction is preferably 150 ppm or less, more preferably 125 ppm or less, much more preferably 100 ppm or less.

The bromine atom content is the amount of a bromine atom contained in a compound containing a bromine atom, such as a bromine molecule and chlorine bromide. When the bromine
20 atom content is higher than 150 ppm, the bromine molecule content of carbonyl chloride becomes higher than 10 ppm and a polycarbonate resin obtained from this carbonyl chloride is apt to have a bromine atom content of more than 0.5 ppm, thereby causing a problem with the quality of the
25 polycarbonate resin. Chlorine having a low content of a bromine atom can be produced by various methods such as electrolytic soda method and Towns method. Out of these, the electrolytic soda method is most economical and common.

30 (carbon monoxide)

The sulfur atom content of carbon monoxide used in the reaction is preferably 10 ppm or less, more preferably 5 ppm or less, much more preferably 0.5 ppm or less. When the sulfur atom content of carbon monoxide is higher than 10 pm,

the sulfur atom content of carbonyl chloride becomes higher than 5 ppm, and a polycarbonate resin obtained from this carbonyl chloride is apt to have a sulfur atom content of more than 100 ppb, thereby causing a problem with the quality of the polycarbonate resin.

Carbon monoxide having a sulfur atom content of 10 ppm or less is obtained by bringing carbon monoxide obtained by reacting coke with oxygen into contact with activated carbon or activated alumina impregnated with a metal added catalyst, such as an oxide and/or a salt of a metal such as copper (Cu), chromium (Cr), vanadium (V) or molybdenum (Mo) and then with a caustic soda aqueous solution, or by bringing it into contact with a caustic soda aqueous solution and then with activated alumina.

15

(specific surface area of catalyst)

The specific surface area of the first catalyst used in the first reactor is 200 to 800 m²/g, preferably 250 to 750 m²/g, more preferably 300 to 700 m²/g.

20

The specific surface area of the second catalyst used in the second reactor is 800 to 1,500 m²/g, preferably 850 to 1,400 m²/g, more preferably 900 to 1,300 m²/g.

When the specific surface area of the first catalyst is represented by X m²/g and the specific surface area of the second catalyst is represented by Y m²/g, (Y-X) m²/g is preferably 100 to 1,300 m²/g, more preferably 200 to 1,000 m²/g, much more preferably 300 to 800 m²/g.

In the present invention, the reaction temperature in the first reactor can be reduced by limiting the specific surface area of the first catalyst used in the first reactor, thereby making it possible to reduce the amount of the formed carbon tetrachloride.

When the reaction temperature in the first reactor becomes low, the reactivity of the catalyst becomes low,

whereby an unreacted chlorine molecule and an unreacted bromine molecule are apt to remain. Thus, when the chlorine molecule and the bromine molecule remain in carbonyl chloride in large quantities, they are contained in the polycarbonate resin finally, thereby deteriorating the quality of a polycarbonate resin product. Therefore, in the present invention, the amounts of the residual chlorine molecule and the residual bromine molecule are reduced by installing the second reactor filled with the second catalyst having a specific surface area of 800 to 1,500 m²/g after the first reactor.

(type of catalyst)

The types of the first catalyst and the second catalyst are not particularly limited. Any porous solid catalyst having the above specific surface area may be used as the catalyst for this reaction. Activated carbon catalysts are often used industrially as the first catalyst and the second catalyst but a porous inorganic catalyst such as zeolite may also be used.

The activated carbon catalysts are widely used because there are a wide variety of the catalysts, their prices and disposal costs are relatively low, and their handling and disposal methods are simple. However, they have a big problem that carbon tetrachloride is readily formed by a side-reaction between activated carbon and a chlorine molecule. When an inorganic catalyst such as zeolite is used, the formation of carbon tetrachloride can be suppressed due to the absence of carbon in the reaction system. However, since the catalyst is inferior to activated carbon in reactivity, even when it is used alone, it is difficult to obtain carbonyl chloride having high purity. Therefore, it is desired to use the inorganic catalyst in combination with the activated carbon catalyst.

The present invention is characterized by finding a combination of the specific surface areas of the first catalyst and the second catalyst as the condition for obtaining carbonyl chloride having high purity by
5 suppressing the by-production of carbon tetrachloride. Further, since high-purity carbonyl chloride can be obtained continuously for a long time industrially by limiting the filled volume ratio and catalyst particle diameters of the first catalyst and the second catalyst, the process for
10 producing the carbonyl chloride will be described as well.

(filled volume ratio of first catalyst and second catalyst)

According to studies conducted by the inventors of the present invention, it was found that when a carbonyl chloride
15 forming reaction is carried out continuously for a long time, the catalyst gradually deteriorates from the upstream side of a gas channel and that a reaction zone gradually moves toward the downstream side. Therefore, it was found that even when the amount of by-produced carbon tetrachloride is
20 small at the start of the reaction, as the reaction rate in the second reactor increases, the amount of the by-produced carbon tetrachloride grows, which is expected to become a big industrial problem. Then, when studies were conducted by changing the volume ratio of the first reactor to the second
25 reactor, it was found that high-quality carbonyl chloride can be obtained for a long time by setting the volume ratio to an appropriate value.

That is, as the condition under which high-purity carbonyl chloride can be produced continuously for a long
30 time, the filled volume ratio of the first catalyst to the second catalyst is preferably $4/6$ to $9/1$. The filled volume ratio is more preferably $5/5$ to $8/2$, particularly preferably $6/4$ to $7/3$.

(particle diameter of catalyst)

The average particle diameters of the first catalyst and the second catalyst are each preferably 0.5 to 5.0 mm, more preferably 1.0 to 4.0 mm, much more preferably 1.5 to 3.0 mm. When the average particle diameters are smaller than 0.5 mm, not only physical bad influences such as the deterioration of handling ease and an increase in pressure loss but also chemical bad influences such as an increase in the amount of by-produced carbon tetrachloride due to high reactivity and the reduction of the life of the catalyst are conceivable. When the average particle diameters are larger than 5.0 mm, reactivity becomes unsatisfactory, whereby the chlorine molecule and the bromine molecule are apt to remain in the obtained carbonyl chloride disadvantageously.

15

(reaction temperature)

The reaction temperature in the first reactor is preferably 300 to 650°C, more preferably 350 to 600°C, much more preferably 400 to 550°C. The reaction temperature in the second reactor is preferably 35 to 90°C, more preferably 40 to 80°C, much more preferably 45 to 70°C.

The first reactor and the second reactor are preferably connected in series. According to the circumstances, the catalysts may be filled in layers from the upstream side of one reactor to the down stream side to prepare a first reactor and a second reactor. Preferably, the reactors have the function of removing reaction heat.

Another reactor may be further installed before the first reactor, between the first reactor and the second reactor, or after the second reactor. The total number of reactors to be installed is preferably 1 to 5, more preferably 2 to 4, much more preferably 2 to 3, particularly preferably 2.

The CO/Cl₂ molar ratio of CO to Cl₂ introduced into the

first reactor is preferably 1.015 to 1.070, more preferably 1.020 to 1.050. When the molar ratio is too high, the yield may lower.

As means of reducing the amount of carbon tetrachloride, it is conceivable to reduce the amounts of CO and Cl₂ gases and the amount of heat generated in the reactors. In this method, productivity is low and it is difficult to obtain a sufficient amount of carbonyl chloride. Another method is to separate carbonyl chloride by distillation. However, this method rarely has the effect of reducing the amounts of the chlorine molecule and the bromine molecule, and high-purity carbonyl chloride cannot be obtained only by this method. Since dedicated equipment is required for the disposal of carbon tetrachloride collected by distillation, this method is not preferred from the industrial point of view.

(reaction pressure)

In the present invention, the reaction pressure in the first reactor and the second reactor is preferably 0.05 to 0.50 MPa (gauge pressure, the same shall apply hereinafter), more preferably 0.06 to 0.40 MPa, much more preferably 0.07 to 0.30 MPa. When the reaction pressure is higher than 0.50 MPa, the reaction rate becomes high, whereby the reaction temperature becomes high with the result that the carbon tetrachloride content of carbonyl chloride may become high. When the reaction pressure is lower than 0.05 MPa, the reaction rate becomes too low, whereby huge amounts of the chlorine molecule and the bromine molecule remain in carbonyl chloride, cannot react even in the second reactor and may remain in carbonyl chloride.

Carbonyl chloride obtained by the above reaction method can be cooled by a condenser through which brine passes and stored in a liquefied carbonyl chloride storage tank.

(quality of carbonyl chloride)

Unless the quality of carbonyl chloride is fully maintained for a long time, it is unworthy of being used for industrial purposes. That is, to use it for industrial purposes, even at a time relatively shortly after the start of using the catalysts (for example, the production of carbonyl chloride is 2.0×10^6 kg/m³ based on 1 m³ of a catalyst) and even after long-term use (for example, the production of carbonyl chloride is 1.6×10^7 kg/m³ based on 1 m³ of a catalyst), high-quality carbonyl chloride must be obtained stably.

According to the process for producing carbonyl chloride of the present invention, at any time when the cumulative production of carbonyl chloride based on 1 m³ of a catalyst is 2.0×10^6 kg/m³ and 1.6×10^7 kg/m³, the carbon tetrachloride content of the obtained carbonyl chloride can be reduced to 20 ppm or less, the chlorine molecule content can be reduced to 20 ppm or less, and the bromine molecule content can be reduced to 10 ppm or less.

Further, at any time when the cumulative production of carbonyl chloride based on 1 m³ of a catalyst is 2.0×10^6 g/m³ and 1.6×10^7 kg/m³, the carbon tetrachloride content of the obtained carbonyl chloride can be reduced to 10 ppm or less, the bromine molecule content can be reduced to 10 ppm or less, and the bromine molecule content can be reduced to 5 ppm or less.

<carbonyl chloride>

Carbonyl chloride obtained by the carbonyl chloride production process of the present invention has a carbon tetrachloride content of 20 ppm or less, a chlorine molecule content of 20 ppm or less and a bromine molecule content of 10 ppm or less.

The carbon tetrachloride content is preferably 15 ppm or less, more preferably 10 ppm or less, particularly preferably 5 ppm or less. The chlorine molecule content is preferably 15 ppm or less, more preferably 10 ppm or less, particularly preferably 5 ppm or less. The bromine molecule content is preferably 8 ppm or less, more preferably 5 ppm or less, particularly preferably 3 ppm or less.

When the carbon tetrachloride content of carbonyl chloride is higher than 20 ppm, the chlorine molecule content is higher than 20 ppm, or the bromine molecule content is higher than 10 ppm, the color of carbonyl chloride becomes worse, a polycarbonate resin having a carbon tetrachloride content of 2 ppm or less, a chlorine content of 1 ppm or less and a bromine content of 0.5 ppm or less is not obtained, and the obtained polycarbonate resin deteriorates in color and metal corrosion resistance and cannot be used in a wide variety of fields.

<polycarbonate resin>

The polycarbonate resin of the present invention can be produced by reacting a dihydric phenol with carbonyl chloride having a carbon tetrachloride content of 20 ppm or less, a chlorine molecule content of 20 ppm or less and a bromine molecule content of 10 ppm or less.

Examples of the dihydric phenol include hydroquinone, resorcinol, 4,4'-biphenol, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane (commonly known as "bisphenol A"), 2,2-bis(4-hydroxy-3-methylphenyl)propane, 2,2-bis(4-hydroxyphenyl)butane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, 2,2-bis(4-hydroxyphenyl)pentane, 4,4'-(p-phenylenediisopropylidene)diphenol,

4,4'-(m-phenylenediisopropylidene)diphenol,
 1,1-bis(4-hydroxyphenyl)-4-isopropylcyclohexane,
 bis(4-hydroxyphenyl)oxide, bis(4-hydroxyphenyl)sulfide,
 bis(4-hydroxyphenyl)sulfoxide,
 5 bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)ketone,
 bis(4-hydroxyphenyl)ester,
 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane,
 bis(3,5-dibromo-4-hydroxyphenyl)sulfone,
 bis(4-hydroxy-3-methylphenyl)sulfide,
 10 9,9-bis(4-hydroxyphenyl)fluorene and
 9,9-bis(4-hydroxy-3-methylphenyl)fluorene. They may be
 used alone or in combination of two or more. Out of these,
 bis(4-hydroxyphenyl)alkanes are preferred, and especially
 bisphenol A (may be abbreviated as "BPA" hereinafter) is
 15 commonly used.

For the manufacture of a polycarbonate from the above
 dihydric phenol and the above carbonyl chloride by
 interfacial polymerization, a catalyst, a terminal capping
 agent and an antioxidant for preventing the oxidation of the
 20 dihydric phenol may be optionally used.

The polycarbonate may be a branched polycarbonate
 obtained by copolymerizing a polyfunctional aromatic
 compound having 3 or more functional groups. Examples of
 the polyfunctional aromatic compound having 3 or more
 25 functional groups include
 1,1,1-tris(4-hydroxyphenyl)ethane and
 1,1,1-tris(3,5-dimethyl-4-hydroxyphenyl)ethane. When the
 polyfunctional compound forming a branched polycarbonate is
 contained, its amount is preferably 0.001 to 1 mol%, more
 30 preferably 0.005 to 0.9 mol%, particularly preferably 0.01
 to 0.8 mol% based on the whole amount of the polycarbonate.

The polymerization reaction of the polycarbonate by
 interfacial polycondensation is generally a reaction between
 a dihydric phenol and carbonyl chloride in the presence of

an acid binder 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.

5 Examples of the organic solvent include halogenated hydrocarbons such as methylene chloride and chlorobenzene. A catalyst such as a tertiary amine, a quaternary ammonium compound or a quaternary phosphonium compound exemplified by triethylamine, tetra-n-butylammonium bromide and
10 tetra-n-butylphosphonium bromide may be used to promote the reaction. The reaction temperature 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
15 agent is generally used. A monofunctional phenol may be used as the terminal capping agent. The monofunctional phenol is preferably phenol, p-tert-butylphenol or p-cumylphenol. Other examples of the monofunctional phenol include monofunctional phenols whose nucleus is substituted by a
20 long-chain alkyl group having 10 or more carbon atoms, such as decyl phenol, dodecyl phenol, tetradecyl phenol, hexadecyl phenol, octadecyl phenol, eicosyl phenol, docosyl phenol and triacontyl phenol. The phenol has the effect of improving fluidity and resistance to hydrolysis. These
25 terminal capping agents may be used alone or in combination of two or more.

 The viscosity average molecular weight of the polycarbonate resin is not particularly limited. However, when the viscosity average molecular weight is lower than
30 1.0×10^4 , mechanical properties such as impact strength deteriorate and when the viscosity average molecular weight is higher than 5.0×10^4 , moldability degrades. Therefore, the viscosity average molecular weight is preferably 1.0×10^4 to 5.0×10^4 , more preferably 1.2×10^4 to 3.0×10^4 , much

more preferably 1.5×10^4 to 2.8×10^4 . In this case, it is possible to mix a polycarbonate having a viscosity average molecular weight outside the above range as long as moldability is maintained. For example, it is possible to
 5 mix a polycarbonate component having a viscosity average molecular weight higher than 5.0×10^4 .

The viscosity average molecular weight M in the present invention is calculated based on the following equation from the specific viscosity (η_{sp}) of a solution containing 0.7 g
 10 of the polycarbonate resin dissolved in 100 ml of methylene chloride at 20°C which is obtained with an Ostwald viscometer based on the following equation.

$$\text{Specific viscosity } (\eta_{sp}) = (t - t_0)/t_0$$

[t_0 is a time (seconds) required for the dropping of methylene chloride and t is a time (seconds) required for the dropping
 15 of a sample solution]

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

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

$$20 \quad c = 0.7$$

To measure the viscosity average molecular weight of the polycarbonate resin, the following procedure is taken. That is, the resin is dissolved in methylene chloride in a weight ratio of 1:20 to 1:30, soluble matter is collected
 25 by cerite filtration, the solution is removed, and the soluble matter is dried completely so as to obtain a methylene chloride-soluble solid. 0.7 g of the solid is dissolved in 100 ml of methylene chloride to measure the specific viscosity (η_{sp}) of the obtained solution at 20°C with an
 30 Ostwald viscometer so as to calculate its viscosity average molecular weight (M) from the above equation.

According to the present invention, a polycarbonate resin having a carbon tetrachloride content of 2 ppm or less, a chlorine atom content of 1 ppm or less and a bromine atom

content of 0.5 ppm or less is obtained by using the above-described carbonyl chloride having reduced contents of impurities. The polycarbonate resin is excellent in color and metal corrosion resistance. When any one of the carbon
5 tetrachloride content, the chlorine atom content and the bromine atom content is outside the above range, a polycarbonate resin which is inferior in color and metal corrosion resistance is obtained.

The carbon tetrachloride content is preferably 1.5 ppm
10 or less, more preferably 1.0 ppm or less. The chlorine atom content is preferably 0.8 ppm or less, more preferably 0.6 ppm or less. The bromine atom content is preferably 0.4 ppm or less, more preferably 0.3 ppm or less.

The polycarbonate resin of the present invention may
15 contain additives which are generally contained in a polycarbonate resin, such as phosphorus-based stabilizer, hindered phenol-based stabilizer, ultraviolet absorbent, flame retardant, bluing agent, light diffuser, antistatic agent, compound having heat ray absorbing capability,
20 inorganic filler, fluidity modifier, antibacterial agent, optical catalyst-based anti-fouling agent, infrared absorbent, photochromic agent, dye and pigment. Another resin and an elastomer may also be used in a small amount as long as the object of the present invention is not impaired.

25

<molded article>

Various molded articles can be produced by molding a pellet obtained by melt extruding the polycarbonate resin of the present invention. A molded article can be generally
30 obtained efficiently by injection molding. Injection molding includes injection compression molding, injection press molding, gas assist injection molding, foam molding (including what comprises the injection of a supercritical fluid), insert molding, in-mold coating molding, insulated

runner molding, quick heating and cooling molding, double-color molding, sandwich molding and super high-speed injection molding which are employed according to purpose. The advantages of these molding techniques are already widely
5 known. The cold runner system and the hot runner system may be selected for molding.

The polycarbonate resin of the present invention may be formed into a profile extrusion molded article, sheet or film by extrusion molding. Inflation, calendering and
10 casting techniques may also be used to mold a sheet or film.

The polycarbonate resin of the present invention is excellent in color, heat stability at the time of molding and metal corrosion resistance and can be used in optical products, automobiles, housings for silicon wafers and
15 electric and electronic equipment, and spectacle lenses. In addition, it can be used in windowpanes for construction machines, buildings, houses and greenhouses. It can also be used in roofs for garages and arcades. It can be further used in illumination lenses, traffic light lenses, lenses
20 of optical equipment, mirrors, spectacles lenses, snow goggles, sound absorbing walls, windshields for motorcycles, nameplates, solar cell covers, solar cell base materials, covers for displays and touch panels. It can also be used in game machines such as pinball machines, circuit covers,
25 chassis and parts such as pin ball carrier guides.

Further, molded articles of the polycarbonate resin of the present invention can be subjected to various surface treatments. The surface treatments such as vapor deposition (such as physical deposition or chemical deposition),
30 plating (such as electroplating, nonelectrolytic plating or hot-dip plating), painting, coating and printing are used to form a new layer on the surface layer of a resin molded article. Techniques which are generally used for polycarbonate resin are employed. The surface treatments

include hard coating, water-repelling and oil-repelling coating, UV absorption coating, infrared absorption coating and metallizing (such as deposition).

5 Examples

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting as long as they do not depart from the gist of the invention. "Parts" in the examples means "parts by weight", and evaluations and molding for evaluations were carried out by the following methods.

(1) Bromine atom content of chlorine

A sample solution prepared by decomposing 1 liter of a chlorine gas with 40 ml of a 20 % NaOH aqueous solution having high purity, diluting the decomposition solution to 10 times and filtering it with a cation removing filter was injected into an anion chromatograph (DX-300 of Nippon Dione Co., Ltd.) to determine the amount of a bromine ion.

(2) Carbon tetrachloride content of carbonyl chloride

1 μ l of carbonyl chloride was injected into a gas chromatograph equipped with an electron capturing detector (Model 263 of Hitachi, Ltd.) to be measured.

(3) Chlorine molecule content and bromine molecule content of carbonyl chloride

A carbonyl chloride gas was injected into a multi-wave type process photometer (Model 3401 of DKK Denki Kagaku Keiki Co., Ltd.) to determine the amounts of a chlorine molecule and a bromine molecule.

(4) Color of carbonyl chloride

The color of carbonyl chloride was checked visually through the internal inspection window of a liquefied storage tank for the formed carbonyl chloride. It was rated based on the following five criteria. As the numeral becomes larger, a tinge of yellow becomes stronger.

Color rating 1: almost colorless

Color rating 2: tinge of yellow is slight

Color rating 3: tinge of yellow is a little strong

Color rating 4: tinge of yellow is strong

5 Color rating 5: tinge of yellow is very strong

For color ratings 1 and 2 out of these ratings, it is judged that the quality of carbonyl chloride is normal and satisfactory. For color rating 3, the quality of carbonyl chloride is slightly abnormal. For color ratings 4 and 5, it is judged that the quality of carbonyl chloride is abnormal. A polycarbonate resin obtained by polymerizing the carbonyl chloride of color rating 4 or 5 greatly deteriorates in metal corrosion resistance.

(5) Carbon tetrachloride content of polycarbonate resin
15 After 5 g of a pellet was put into a 120 ml stainless steel container, the container was stoppered tightly, and the pellet was heated at 250°C for 2 hours, 1 ml of a head space gas was injected into a gas chromatograph equipped with an electron capturing detector (Model 263 of Hitachi, Ltd.)
20 to measure the carbon tetrachloride content of the polycarbonate resin.

(6) Chlorine atom content and bromine atom content of polycarbonate resin

A plate obtained by thermally compression molding
25 polymer powders at 190°C was used to measure the intensity of a chlorine atom and the intensity of a bromine atom with fluorescent X-ray (RIX2000 of Rigaku Denki Kogyo Co., Ltd.).

(7) Color of polycarbonate resin molded article

The YI value of a 2.0 mm-thick molded plate obtained
30 by injection molding (SG260M-HP of Sumitomo Heavy Industries, Ltd.) at a cylinder temperature of 310°C was calculated from X, Y and Z values obtained by measuring transmitted light with the Z-1001DP color-difference meter of Nippon Denshoku Co., Ltd. based on the following equation in accordance with

ASTM-E1925. As the YI value becomes larger, a tinge of yellow of the molded plate becomes stronger.

$$YI = [100(1.28X - 1.06Z)]/Y$$

(8) Molding heat stability of polycarbonate resin

5 The YI value of a molded plate having the same shape as in the above evaluation (7) and formed from a resin which was retained in the cylinder of a molding machine for 10 minutes was measured in the same manner as in (7). The difference ΔYI was obtained by subtracting the YI value of
10 the test sample before residence from the YI value of the test sample after residence.

(9) Evaluation of mold corrosion resistance of polycarbonate resin at the time of molding

200 transparent head lamp lenses shown in Fig. 1 were
15 molded continuously at a cylinder temperature of 310°C and a molded temperature of 80°C with an injection molding machine (SG260M-HP of Sumitomo Heavy Industries, Ltd.) and then, the surface of the metal mold was subjected to a moist heat treatment at a relative humidity of 100 % and a
20 temperature of 120°C for 24 hours to observe the corrosion of the surface. The degree of corrosion was evaluated based on the following five criteria. As the numeral becomes larger, the degree of corrosion becomes higher.

Corrosion rating 1: almost not corroded

25 Corrosion rating 2: slightly corroded

Corrosion rating 3: more corroded

Corrosion rating 4: much more corroded

Corrosion rating 5: greatly corroded

For corrosion ratings 1 and 2 out of these ratings,
30 it is judged that the quality of carbonyl chloride is satisfactory and the degree of corrosion is acceptable. For corrosion rating 3, corrosion slightly proceeds. For corrosion ratings 4 and 5, it is judged that corrosion proceeds to such an extent that the quality of carbonyl

chloride is abnormal. When the polycarbonate resin of corrosion rating 4 or 5 is molded, the screw of a molding machine or the surface of a metal mold is easily corroded with the result of poor quality.

5

Example 1

(production of carbonyl chloride)

40°C cooling water was let pass on the shell side of a multi-tubular type reactor having the function of removing reaction heat, and a first reactor filled with coconut shell
10 activated carbon (first catalyst) having a specific surface area of 400 m²/g and an average particle diameter of 2.5 mm was installed on the tube side.

On the downstream side of the first reactor, 40°C
15 cooling water was let pass on the shell side of a multi-tubular type reactor having the function of removing reaction heat, and a second reactor filled with coconut shell activated carbon (second catalyst) having a specific surface area of 900 m²/g and an average particle diameter of 3.5 mm was
20 installed on the tube side.

A condenser through which -25°C brine was let pass and a liquefied carbonyl chloride storage tank were installed on the downstream side of the second reactor.

These apparatuses were connected in series to obtain
25 carbonyl chloride by letting 10.30 Nm³/hr of a CO gas and 10.00 Nm³/hr of a Cl₂ gas in a CO/Cl₂ molar ratio of 1.030 pass from the first reactor at a pressure of 0.15 MPa (gauge pressure). The filled volume ratio of the first catalyst to the second catalyst was 6.7/3.3, the reaction temperature
30 of the first reactor was 520°C, and the reaction temperature of the second reactor was 45°C.

(life of catalyst)

Further, to confirm the lives of the catalysts, the

quality of carbonyl chloride when the cumulative production of carbonyl chloride (based on 1 m³ of a catalyst) shortly after the start of aeration became 2.0×10^6 kg/m³ (Table 1) and the quality of carbonyl chloride when the cumulative production of carbonyl chloride (based on 1 m³ of catalyst) after long-term operation became 1.6×10^7 kg/m³ were checked and shown in Table 2.

(production of polycarbonate resin)

Then, a polycarbonate resin was produced from the obtained carbonyl chloride. 219.4 parts of ion exchange water and 40.2 parts of a 48% sodium hydroxide aqueous solution were fed to a reactor equipped with a thermometer, stirrer and reflux condenser, 57.5 parts (0.252 mol) of 2,2-bis(4-hydroxyphenyl)propane and 0.12 part of hydrosulfite were dissolved in the resulting solution, 181 parts of methylene chloride was added to the resulting solution, and 28.3 parts of the above carbonyl chloride was blown into the reactor at 15 to 25°C under agitation over 40 minutes. After carbonyl chloride was blown, 7.2 parts of a 48 % sodium hydroxide aqueous solution and 2.42 parts of p-tert-butylphenol were added to the resulting product, the obtained product was started to be stirred and emulsified, 0.06 part of triethylamine was added and further stirred at 28 to 33°C for 1 hour, and the reaction was terminated.

After the end of the reaction, the product was diluted with methylene chloride, rinsed in water, made acidic with hydrochloric acid and rinsed in water, and when the conductivity of a water phase became equal to that of ion exchange water, this methylene chloride solution was added dropwise to the hot water of a kneader having an isolated chamber with a foreign matter take-out port in a bearing portion to evaporate methylene chloride so as to obtain polycarbonate resin powders having a viscosity average

molecular weigh of 15,100.

The powders were dried at 145°C for 6 hours, and 0.004 wt% of tris(2,4-di-tert-butylphenyl)phosphite and 0.06 wt% of monoglyceride stearate were added to the powders. Then, 5 the powders were melt kneaded by means of a vented double-screw extruder (KTX-46 of Kobe Steel, Ltd.) while deaeration was carried out at a cylinder temperature of 240°C to obtain a polycarbonate resin pellet. The evaluation results of the obtained carbonyl chloride and polycarbonate 10 resin are shown in Table 1.

Example 2

Carbonyl chloride and a polycarbonate resin pellet were obtained in the same manner as in Example 1 except that 15 the filled volume ratio of the first catalyst to the second catalyst was changed to 9.1/0.9. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after 20 long-term operation are shown in Table 2.

Example 3

Carbonyl chloride and a polycarbonate resin pellet were obtained in the same manner as in Example 1 except that 25 the filled volume ratio of the first catalyst to the second catalyst was changed to 3.3/6.7. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after 30 long-term operation are shown in Table 2.

Example 4

Carbonyl chloride and a polycarbonate resin pellet

were obtained in the same manner as in Example 1 except that the average particle diameter of the first catalyst was changed to 5.5 mm. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after long-term operation are shown in Table 2.

Example 5

A reaction for obtaining carbonyl chloride was carried out under the same conditions as in Example 1 except that activated carbon having a specific surface area of $600 \text{ m}^2/\text{g}$ was used in the first reactor and activated carbon having a specific surface area of $1,200 \text{ m}^2/\text{g}$ was used in the second reactor to obtain liquefied carbonyl chloride. A polycarbonate resin pellet was obtained in the same manner as in Example 1. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after long-term operation are shown in Table 2.

Example 6

A reaction for obtaining carbonyl chloride was carried out under the same conditions as in Example 1 except that activated carbon having a specific surface area of $1,000 \text{ m}^2/\text{g}$ was used in the second reactor and the reaction pressure was changed to 0.40 MPa (gauge pressure) to obtain liquefied carbonyl chloride. A polycarbonate resin pellet was obtained in the same manner as in Example 1. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after long-term operation are shown in Table 2.

Example 7

A reaction for obtaining carbonyl chloride was carried out under the same conditions as in Example 6 except that
5 the reaction pressure was changed to 0.51 MPa (gauge pressure) to obtain liquefied carbonyl chloride. A polycarbonate resin pellet was obtained in the same manner as in Example 6. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table
10 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after long-term operation are shown in Table 2.

Example 8

15 A reaction for obtaining carbonyl chloride was carried out under the same conditions as in Example 5 except that a zeolite catalyst (specific surface area of $500 \text{ m}^2/\text{g}$, average particle diameter of 2.0 mm) was used as the first catalyst to obtain liquefied carbonyl chloride. A polycarbonate
20 resin pellet was obtained in the same manner as in Example 5. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after long-term operation are shown in
25 Table 2.

Comparative Example 1

A reaction for obtaining carbonyl chloride was carried out under the same conditions as in Example 1 except that
30 activated carbon having a specific surface area of $900 \text{ m}^2/\text{g}$ was used as the first catalyst to obtain liquefied carbonyl chloride. A polycarbonate resin pellet was obtained in the same manner as in Example 1. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown

in Table 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after long-term operation are shown in Table 2.

5 Comparative Example 2

A reaction for obtaining carbonyl chloride was carried out under the same conditions as in Example 1 except that activated carbon having a specific surface area of 150 m²/g was used as the first catalyst to obtain liquefied carbonyl chloride. A polycarbonate resin pellet was obtained in the same manner as in Example 1. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table 1. Further, the evaluation results of the obtained carbonyl chloride and polycarbonate resin after long-term operation are shown in Table 2.

Comparative Example 3

A reaction for obtaining carbonyl chloride was carried out by using only the first catalyst without using the second catalyst in Example 1 to obtain liquefied carbonyl chloride. A polycarbonate resin pellet was obtained in the same manner as in Example 1. The evaluation results of the obtained carbonyl chloride and polycarbonate resin are shown in Table 1. Since the quality of carbonyl chloride at the start of operation was unsatisfactory in this experiment, long-term operation was not carried out.

Table 1
(quality when the cumulative production of carbonyl chloride is 2.0×10^6 kg/m³)
carbonyl chloride forming reaction

in chlorine		carbonyl chloride forming reaction					
content of bromine		first reaction catalyst		second reaction catalyst		volume ratio of first reaction/second reaction	reaction pressure
		specific surface area	average particle diameter	specific surface area	average particle diameter		
wtppm		m ² /g	mm	m ² /g	mm	filled volume ratio	MPa (gauge pressure)
Ex. 1	120	400	2.5	900	3.5	6.7 / 3.3	0.15
Ex. 2	120	400	2.5	900	3.5	9.1 / 0.9	0.15
Ex. 3	120	400	2.5	900	3.5	3.3 / 6.7	0.15
Ex. 4	120	400	5.5	900	3.5	6.7 / 3.3	0.15
Ex. 5	120	600	2.5	1200	3.5	6.7 / 3.3	0.15
Ex. 6	120	400	2.5	1000	3.5	6.7 / 3.3	0.40
Ex. 7	120	400	2.5	1000	3.5	6.7 / 3.3	0.51
Ex. 8	120	500 (zeolite catalyst)	2.0	1200	3.5	6.7 / 3.3	0.15
C. Ex. 1	120	900	2.5	900	3.5	6.7 / 3.3	0.15
C. Ex. 2	120	150	2.5	900	3.5	6.7 / 3.3	0.15
C. Ex. 3	120	400	2.5	none	none		0.15

Ex.: Example C.Ex.: Comparative Example

Table 1 (continued)

(quality when the cumulative production of carbonyl chloride is $2.0 \times 10^6 \text{ kg/m}^3$)

	quality of carbonyl chloride				color
	carbon tetrachloride content	chlorine molecule content	bromine molecule content	Visual rating (1~5)	
	wtppm	wtppm	wtppm		
Ex. 1	9	5	3	1	
Ex. 2	9	10	5	1	
Ex. 3	9	3	2	1	
Ex. 4	8	20	7	2	
Ex. 5	15	4	2	1	
Ex. 6	15	6	2	1	
Ex. 7	30	4	2	1	
Ex. 8	0.5	10	5	2	
C. Ex. 1	85	6	2	1	
C. Ex. 2	8	35	10	4	
C. Ex. 3	9	500	25	5	

Ex.: Example C.Ex.: Comparative Example

Table 1 (continued)

(quality when the cumulative production of carbonyl chloride is 2.0×10^6 kg/m³)

	quality of polycarbonate resin					
	carbon tetrachloride content	chlorine atom content	bromine atom content	color of molded article	molding heat stability	mold corrosion resistance
	wtppm	wtppm	wtppm	YI	ΔYI	Visual rating (1~5)
Ex. 1	0.9	0.4	0.2	0.5	0.1	1
Ex. 2	0.9	0.7	0.5	0.5	0.1	1
Ex. 3	0.9	0.4	0.2	0.5	0.1	1
Ex. 4	0.9	1.5	0.5	0.7	0.4	1
Ex. 5	1.6	0.3	0.1	0.3	0.1	2
Ex. 6	1.7	0.3	0.1	0.3	0.1	2
Ex. 7	2.6	0.2	0.1	0.3	0.1	3
Ex. 8	0.1	0.2	0.1	0.6	0.3	1
C. Ex. 1	5.7	0.3	0.1	0.3	0.5	4
C. Ex. 2	0.9	2.3	1.1	1.9	1.2	3
C. Ex. 3	0.8	6	2	5.4	2.5	4

Ex.: Example C.Ex.: Comparative Example

Table 2

(quality when the cumulative production of carbonyl chloride is 1.6×10^7 kg/m³)

	in chlorine content of bromine	carbonyl chloride forming reaction					
		first reaction catalyst		second reaction catalyst		volume ratio of first reaction/second reaction	reaction pressure
		specific surface area	average particle diameter	specific surface area	average particle diameter		
	wtppm	m ² /g	mm	m ² /g	mm	filled volume ratio	MPa (gauge pressure)
Ex. 1	120	400	2.5	900	3.5	6.7 / 3.3	0.15
Ex. 2	120	400	2.5	900	3.5	9.1 / 0.9	0.15
Ex. 3	120	400	2.5	900	3.5	3.3 / 6.7	0.15
Ex. 4	120	400	5.5	900	3.5	6.7 / 3.3	0.15
Ex. 5	120	600	2.5	1200	3.5	6.7 / 3.3	0.15
Ex. 6	120	400	2.5	1000	3.5	6.7 / 3.3	0.40
Ex. 7	120	400	2.5	1000	3.5	6.7 / 3.3	0.51
Ex. 8	120	500 (zeolite catalyst)	2.0	1200	3.5	6.7 / 3.3	0.15
C. Ex. 1	120	900	2.5	900	3.5	6.7 / 3.3	0.15
C. Ex. 2	120	150	2.5	900	3.5	6.7 / 3.3	0.15
C. Ex. 3	120	400	2.5	none	none	-	-

Ex.: Example C.Ex.: Comparative Example

Table 2 (continued)

(quality when the cumulative production of carbonyl chloride is $1.6 \times 10^7 \text{ kg/m}^3$)

	quality of carbonyl chloride				color
	carbon tetrachloride content	chlorine molecule content	bromine molecule content		
	wtppm	wtppm	wtppm	Visual rating (1~5)	
Ex. 1	7	6	3	1	
Ex. 2	8	34	12	4	
Ex. 3	25	3	2	1	
Ex. 4	8	25	8	3	
Ex. 5	13	6	3	1	
Ex. 6	14	9	3	2	
Ex. 7	27	5	2	1	
Ex. 8	0.5	15	6	2	
C. Ex. 1	80	7	2	1	
C. Ex. 2	12	56	19	5	
C. Ex. 3	-	-	-	-	

Ex.: Example C.Ex.: Comparative Example

Table 2 (continued)

(quality when the cumulative production of carbonyl chloride is 1.6×10^7 kg/m³)

quality of polycarbonate resin						
carbon tetrachloride content	chlorine atom content	bromine atom content	color of molded article	molding heat stability	mold corrosion resistance	
wtppm	wtppm	wtppm	YI	ΔYI	Visual rating (1~5)	
Ex. 1	0.8	0.4	0.2	0.5	0.1	1
Ex. 2	0.8	2.1	1.1	2.0	1.1	1
Ex. 3	2.3	0.3	0.2	0.5	0.1	3
Ex. 4	0.9	1.4	0.5	0.7	0.4	1
Ex. 5	1.5	0.3	0.1	0.3	0.1	2
Ex. 6	1.7	0.4	0.1	0.3	0.1	2
Ex. 7	2.4	0.2	0.1	0.3	0.1	3
Ex. 8	0.1	0.3	0.2	0.8	0.4	1
C. Ex. 1	5.5	0.3	0.1	0.3	0.5	4
C. Ex. 2	1.0	3.3	1.3	2.2	1.3	3
C. Ex. 3	-	-	-	-	-	-

Ex.: Example C.Ex.: Comparative Example

Effect of the Invention

According to the process for producing carbonyl chloride of the present invention, carbonyl chloride which has a low carbon tetrachloride content, a low chlorine molecule content and a low bromine molecule content and has a good color is obtained. In the process for producing carbonyl chloride of the present invention, the catalysts rarely deteriorate, thereby making long-term continuous operation possible.

According to the present invention, a polycarbonate resin which rarely contains a metal corrosive substance and has a good color and excellent molding heat stability can be provided.

Industrial Applicability

Since the polycarbonate resin of the present invention has excellent molding heat stability and metal corrosion resistance, it can be used in optical products, automobiles, housings for silicon wafers and electric and electronic equipment, and spectacle lenses.

CLAIMS

1. A process for producing carbonyl chloride, comprising the steps of:
 - 5 (i) bringing chlorine and carbon monoxide into contact with a first catalyst having a specific surface area of 200 to 800 m²/g; and
 - (ii) bringing the obtained product into contact with a second catalyst having a specific surface area of 800 to
10 1,500 m²/g.
2. The production process according to claim 1, wherein the filled volume ratio of the first catalyst to the second catalyst is 4/6 to 9/1.
15
3. The production process according to claim 1, wherein the first catalyst and the second catalyst are both activated carbon.
- 20 4. The production process according to claim 1, wherein the average particle diameters of the first catalyst and the second catalyst are each 0.5 to 5.0 mm.
5. The production process according to claim 1, wherein
25 the average particle diameters of the first catalyst and the second catalyst are each 1.0 to 4.0 mm.
6. The production process according to claim 1, wherein the above contact is carried out at a pressure of 0.05 to
30 0.50 MPa (gauge pressure).
7. The production process according to claim 1, wherein the obtained carbonyl chloride has a carbon tetrachloride content of 20 ppm or less, a chlorine molecule content of

20 ppm or less and a bromine molecule content of 10 ppm or less even when the cumulative production of carbonyl chloride based on 1 m³ of a catalyst is 2.0×10^6 kg/m³ and 1.6×10^7 kg/m³.

5

8. The production process according to claim 1, wherein the obtained carbonyl chloride has a carbon tetrachloride content of 10 ppm or less, a chlorine molecule content of 10 ppm or less and a bromine molecule content of 5 ppm or less when the cumulative production of carbonyl chloride based on 1 m³ of a catalyst is 2.0×10^6 kg/m³ and 1.6×10^7 kg/m³.

9. Carbonyl chloride having a carbon tetrachloride content of 20 ppm or less, a chlorine molecule content of 20 ppm or less and a bromine molecule content of 10 ppm or less.

10. A process for producing a polycarbonate resin by reacting a dihydric phenol with the carbonyl chloride of claim 9.

11. A polycarbonate resin having a carbon tetrachloride content of 2 ppm or less, a chlorine atom content of 1 ppm or less and a bromine atom content of 0.5 ppm or less.

12. A molded article obtained by melt molding the polycarbonate resin of claim 11.