

DESCRIPTION

Title of Invention

METHOD FOR PRODUCING ETHYLENE CARBONATE AND ETHYLENE GLYCOL

Field of the Invention:

[0001] The present invention relates to a method for producing ethylene carbonate and/or ethylene glycol.

Description of the Related Art:

[0002] Ethylene carbonate is used, for example, as a solvent for various high molecular weight compounds, a reaction solvent for various chemical reactions, a solvent for an electrolyte solution (electrolytic solution) for lithium ion secondary batteries, an extractant, a foaming agent, and a lubricating oil stabilizer. Usually, ethylene carbonate is synthesized by reacting ethylene oxide and carbon dioxide at a high temperature and a high pressure. Therefore, diols, which include, for example, ethylene glycol and diethylene glycol originating from the materials for the synthesis, are contained in ethylene carbonate. Further, a minute amount of water is also contained in ethylene carbonate together with the impurities as described above. The water reacts with ethylene carbonate to further produce ethylene glycol.

[0003] It is preferable that ethylene carbonate, which is used as various types of solvents, does not contain any impurity to the utmost extent. Various methods, which include, for example, the distillation method and the crystallization method, have been

suggested as methods for purifying ethylene carbonate.

The distillation method is the purification method which is industrially carried out most widely. However, ethylene carbonate has a boiling point of 246°C (atmospheric pressure) which is high. Therefore, when ethylene carbonate is purified in accordance with the distillation method, even if the distillation is performed at a reduced pressure, then any thermal degradation or deterioration is caused, and ethylene carbonate tends to react with diols and water to form high molecular weight compounds. According to investigations performed by the present inventors, the following fact has been revealed. That is, the bonds of the high molecular weight ethylene glycol compounds are partially cut to return to diols. Therefore, even when the distillation is performed, diols consequently remain in an amount of about 100 ppm in ethylene carbonate. Further, the distillation method requires the energy corresponding to the latent heat of vaporization or evaporation of the concerning substance, in addition to which it is also necessary to increase the reflux ratio. Therefore, the consumed energy is extremely large as compared with the crystallization method in which it is enough to perform only the cooling by means of the removal of the sensible heat.

[0004] The crystallization method is the purification method which utilizes the fact that impurity components, which are not crystallized at a certain temperature when the objective component is crystallized, are not mixed into crystals. The crystallization method makes it possible to perform the purification by means of only the operation including the crystallization by cooling and the dissolution by slight warming. Therefore, the degradation is hardly

caused by the side reaction, and the consumed energy is small. Further, Patent Document 1 discloses that ethylene carbonate having a high purity of not less than 99.999% can be obtained when a crystallization method described in this patent document is applied.

[0005] However, when ethylene carbonate is purified by using the crystallization method, a slight amount of colored component is present in purified ethylene carbonate. The colored component causes any problem especially in the case of the way of use for an electrolyte solution for a lithium ion secondary battery or the like in which the high purity is required.

According to investigations performed by the present inventors, the following fact has been progressively revealed. That is, the colored component as described above is not removed, for example, by means of such a method (Patent Document 2 and Patent Document 3) that a part of a reaction solution containing a catalyst is obtained in order to recover the catalyst, to which water is added so that the solution is circulated to the process after recovering the catalyst. The colored component remains in the catalyst solution to be circulated to the process, and the colored component is concentrated as the operation is continuously performed.

[0006] On the other hand, a method for producing ethylene glycol is known, wherein ethylene oxide and carbon dioxide are reacted at a high temperature and a high pressure to obtain an ethylene carbonate-producing reaction solution to which water is further added to cause a hydrolysis reaction so that ethylene glycol is produced thereby (Patent Document 4, Patent Document 5, Patent Document 6 and Patent Document 7). The process described above causes such a problem that

an outlet control valve or the like is clogged up or blocked in a hydrolysis reaction vessel (reaction tank) when the continuous operation is performed while circulating and using a catalyst.

[0007]

Patent Document 1: Japanese Patent Application Laid-open No. 2007-284427

Patent Document 2: United Kingdom Patent No. 2098985

Patent Document 3: Japanese Patent Application Laid-open No. 2004-262767

Patent Document 4: Japanese Patent Publication No. 55-47617

Patent Document 5: Japanese Patent Application Laid-open No. 59-13741

Patent Document 6: Japanese Patent Application Laid-open No. 2000-128814

Patent Document 7: Japanese Patent Application Laid-open No. 2004-196722

SUMMARY OF THE INVENTION

[0008] An object of the present invention is to provide a method for producing ethylene carbonate in which a colored component contained in ethylene carbonate as described above is removed, and provide a method for producing ethylene glycol which makes it possible to perform the operation stably for a long period of time while avoiding the clog-up or blockade in an ethylene glycol production process as described above.

[0009] As a result of diligent investigations performed by the present inventors in order to achieve the foregoing object, the following fact has been found out. That is, ethylene carbonate, from

which any colored component is removed, is produced in accordance with a method for producing ethylene carbonate based on a process (referred to herein as "EC production process" in some cases) comprising the steps of obtaining a reaction solution containing ethylene carbonate by reacting carbon dioxide and ethylene oxide in the presence of a catalyst and purifying produced ethylene carbonate by means of crystallization, the method comprising extracting a part of the ethylene carbonate-producing reaction solution (referred to herein as "carbonation reaction solution (carbonate-producing reaction solution)" in some cases), adding water to the extracted solution in an amount of not less than 20 times by weight an amount of the catalyst dissolved in the extracted solution to deposit undissolved matters, removing the deposited undissolved matters from the extracted solution, and then circulating the resultant solution to the process. Further, the present inventors have found out the fact that any clog-up or any blockade is not caused at an outlet control valve of a reaction vessel (reaction tank) in a hydrolysis step even when the operation is continuously performed for 1 year in accordance with a process of producing ethylene glycol by further adding water to the carbonation reaction solution (hereinafter referred to as "hydrolysis step" in some cases), the process comprising extracting a part of the carbonation reaction solution, adding water to the extracted solution in an amount of not less than 20 times by weight an amount of the catalyst dissolved in the extracted solution to deposit undissolved matters, removing the deposited undissolved matters from the extracted solution, and then circulating the resultant solution to the process. Thus, the present

invention has been completed.

[0010] That is, the present invention has the following features.

(1) A method for producing ethylene carbonate comprising obtaining a reaction solution containing ethylene carbonate by reacting carbon dioxide and ethylene oxide in the presence of a catalyst and purifying produced ethylene carbonate by means of crystallization, the method comprising extracting a solution containing the catalyst from the reaction solution, adding water to the extracted solution in an amount of not less than 20 times by weight an amount of the catalyst dissolved in the extracted solution to deposit undissolved matters, removing the deposited undissolved matters from the extracted solution, and then circulating the resultant solution to the reaction solution.

(2) The method according to (1), wherein the solution containing the catalyst is a part of an outlet solution obtained from a reactor for reacting carbon dioxide and ethylene oxide to produce ethylene carbonate.

(3) A method for producing ethylene glycol comprising obtaining a reaction solution containing ethylene carbonate and ethylene glycol by reacting carbon dioxide, ethylene oxide, and water in the presence of a catalyst, and converting ethylene carbonate to ethylene glycol by further adding water to the obtained reaction solution, the method comprising extracting a solution containing the catalyst from the reaction solution, adding water to the extracted solution in an amount of not less than 20 times by weight an amount of the catalyst dissolved in the extracted solution to deposit

undissolved matters, removing the deposited undissolved matters from the extracted solution, and then circulating the resultant solution to the reaction solution.

(4) The method according to (3), wherein the solution containing the catalyst is a part of an outlet solution obtained from a reactor for reacting carbon dioxide, ethylene oxide, and water to produce ethylene carbonate and ethylene glycol and/or a part of an outlet solution obtained from a reactor for converting ethylene carbonate to ethylene glycol by adding water to the obtained reaction solution.

(5) The method according to any one of (1) to (4), wherein the undissolved matters are removed by means of static separation, filtrating separation, or adsorptive removal with an adsorptive substance.

(6) The method according to any one of (1) to (5), wherein the catalyst is quaternary phosphonium iodide or bromide.

(7) An ethylene carbonate which has a Hazen number of not more than 10 in relation to a color and which has a purity of not less than 99.999%.

(8) A non-aqueous electrolyte solution which contains the ethylene carbonate as defined in (7).

[0011] According to the present invention, the method for producing ethylene carbonate is provided, wherein ethylene carbonate has the high purity, from which the colored component is removed. Further, the method for producing ethylene glycol is provided, wherein the operation can be performed stably without causing any clog-up or any blockade even when the operation is performed

continuously for a long term.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] (1) About colored component

The colored component contained in ethylene carbonate, which is intended to be removed in the method for producing ethylene glycol according to the present invention, is a substance which emits the fluorescence when the substance is illuminated with the ultraviolet light. When the origin of the presence of the substance is traced in accordance with the fluorometric analysis in the process for producing ethylene carbonate of the present invention including the steps of producing ethylene carbonate by reacting carbon dioxide and ethylene oxide in the presence of the catalyst and purifying produced ethylene carbonate by means of the crystallization, then the substance already exists in a drain of an outlet gas obtained from an oxidation reactor for producing the raw material of ethylene oxide, the substance thereafter passes through an ethylene oxide absorption tower and an ethylene oxide stripping tower, and the substance is also contained in ethylene oxide as the raw material for the EC production process of the present invention. In the EC production process, the colored component is circulated or cycled to the process together with the catalyst, and the colored component is concentrated.

[0013] When it is intended to recover produced ethylene carbonate at a high purity in accordance with the crystallization method, then the concentrated colored component is mixed into

ethylene carbonate as the product, and a reddish color is brought about. As a result of the structural analysis, the colored component is composed of components consisting of polyethylene glycol, polyethylene, and aromatic compound. The colored component is soluble in a polar solvent such as methanol or the like. However, the solubility in water is low. Therefore, the substance can be deposited (precipitated) and removed when a certain amount of water is added.

[0014] (2) Method for producing ethylene carbonate

The method for producing ethylene carbonate of the present invention is based on the process including the steps of obtaining a reaction solution containing ethylene carbonate by reacting carbon dioxide and ethylene oxide in the presence of the catalyst (referred to herein as "carbonation reaction (carbonate-producing reaction)" in some cases) and purifying produced ethylene carbonate by means of the crystallization.

[0015] It is appropriate that the catalyst, which is usable in the ethylene carbonate-producing reaction described above, is appropriately selected from known catalysts to be used, including, for example, bromides or iodides of alkali metals (those described, for example, in Japanese Patent Publication No. 38-23175), halides of alkaline earth metals (those described, for example, in United States Patent No. 2,667,497), alkylamines, quaternary ammonium salts (those described, for example, in United States Patent No. 2,773,070), organic stannum, germanium, or tellurium compounds (those described, for example, in Japanese Patent Application Laid-open No. 57-183784), and halogenated organic phosphonium salts (those described, for

example, in Japanese Patent Application Laid-open No. 58-126884). In particular, it is preferable to use bromides or iodides of alkali metals or phosphonium salts. Preferred examples include, for example, potassium iodides, potassium bromides, quaternary phosphonium iodides or quaternary phosphonium bromides exemplified, for example, by triphenylmethylphosphonium iodide, triphenylpropylphosphonium iodide, triphenylbenzylphosphonium iodide, tributylmethylphosphonium iodide, and bromides thereof. A compound, which forms alkali metal carbonate, may be also used in combination with phosphonium salt. Alkali metal carbonate suppresses production of any by-product other than ethylene glycol and ethylene carbonate in the carbonation reaction, which is preferred. Potassium salt having a large solubility is preferred as the alkali metal. A preferred example, which is adoptable when the catalyst is used in combination, is as described in Japanese Patent Application Laid-open No. 2000-128814.

[0016] It is also allowable that ethylene oxide having a high purity, which is commercially available, is used as ethylene oxide to be used as the raw material for the carbonation reaction of the present invention. However, as described, for example, in Ullmanns Encyclopedia of Industrial Chemistry, 5th Ed., vol. A10, from p. 117, it is also possible to use, after the purification to be performed, for example, as described below, a product which is synthesized by performing a reaction such that a gas, which contains the main components of ethylene as a raw material, oxygen, and methane as a dilution gas, is allowed to pass through a multitubular reactor charged with a silver catalyst. Usually, the selectivity of ethylene

to ethylene oxide is about 80%. About 20% of the residual is converted into carbon dioxide and water in accordance with the complete oxidation reaction. The oxidation reaction gas, which flows out from the reactor, is composed of, for example, produced ethylene oxide, unreacted ethylene, carbonic acid gas, oxygen, and dilution gas. Produced ethylene oxide is absorbed into the liquid phase in an absorption tower to use water as an absorption liquid. Ethylene oxide, which is absorbed in the absorption liquid, is distilled or stripped in an ethylene oxide stripping tower, and ethylene oxide is recovered from the tower top as an aqueous solution of ethylene oxide having a high concentration. Further, the dehydration and the purification are performed in a distillation tower. The aqueous solution of high concentration ethylene oxide, which is obtained from the tower top as described above, can be also directly used as the raw material.

[0017] The carbonation reaction can be performed by using any arbitrary apparatus. For example, a bubble tower, which has, at an intermediate position, a liquid circulation conduit provided with a heat exchanger for removing the heat and a pump for the circulation, is used to control the reaction temperature by circulating the reaction solution contained in the tower via the liquid circulation conduit. The reaction can be performed continuously by continuously supplying the raw materials of ethylene oxide and carbon dioxide and the catalyst from the tower bottom. It is also preferable to use a reactor provided with an ejector type nozzle as disclosed in Japanese Patent Application Laid-open No. 11-269110. The reaction temperature is usually 70 to 200°C. However, the reaction temperature is

preferably 100°C to 170°C.

[0018] The reaction pressure is usually 0.6 to 5.0 MPa.

However, the reaction pressure is preferably 1.0 to 3.0 MPa. Water may be added to the carbonation reaction of the present invention.

In the presence of water, ethylene oxide is converted into not only ethylene carbonate but also ethylene glycol. Therefore, the reaction is easily advanced even in the case of a supply amount of carbon dioxide of not more than an equimolar amount with respect to ethylene oxide. The supply molar ratio of carbon dioxide with respect to ethylene oxide is usually not more than 5 and preferably 0.5 to 3.0.

[0019] The supply molar ratio of water with respect to ethylene oxide is usually not more than 10 and preferably 0.5 to 5.0. It is inefficient to completely react ethylene oxide in the bubble tower. Therefore, it is also preferable that a tubular reactor is arranged after the bubble tower, and ethylene oxide in the solution or liquid is further reacted. In this procedure, the amount of addition of the catalyst is 1/1000 to 1/20 and preferably 1/200 to 1/50 in molar ratio with respect to ethylene oxide. A part of the reaction solution obtained in the carbonation reaction may be fed to the purification step of purifying ethylene carbonate as described later on, and the remaining may be preferably circulated to the carbonation reactor by performing the operation for removing the colored component as described later on after performing the operation for recovering the catalyst as described later on. Alternatively, the operation for recovering the catalyst and the operation for removing the colored component may be performed as distinct operations. The operation for recovering the catalyst, which is performed in order to

avoid the degradation or deterioration of the catalyst, is exemplified, for example, by methods described, for example, in Japanese Patent Application Laid-open Nos. 2004-262767, 2004-284976, and 2004-292384.

[0020] In general, a method for separating ethylene carbonate from the carbonation reaction solution by means of the crystallization is available, in which crude ethylene carbonate crystals are produced by cooling the carbonation reaction solution. As for the cooling method, the cooling can be performed in accordance with a known method. Specifically, for example, it is possible to use a method as described in Japanese Patent Application Laid-open No. 7-89905, wherein the crystals are deposited on cold perpendicular spacing walls, followed by being warmed so that parts of crystals are melted, which are allowed to flow downwardly to be subjected to the separation, and thus crystals having a raised purity are recovered. On the other hand, a countercurrent contact method is also known as a continuous crystallization method (described, for example, in Japanese Patent Application Laid-open No. 2007-284427, United Kingdom Patent No. 1086028, and "Separation Technology" (The Society of Separation Process Engineers, Japan), Vol. 35, No. 6, pp. 45-49 (2005)). The countercurrent contact method is such a method that the purity of ethylene carbonate is raised by means of the contact between crystals of ethylene carbonate and a liquid.

[0021] In the EC production process of the present invention, the solution containing the catalyst in the process is extracted from the reaction solution and then water is added to the extracted solution in an amount of not less than 20 times by weight of an

amount of the catalyst dissolved in the extracted solution to deposit undissolved matters. By removing the deposited undissolved matters, the colored component is removed (this operation is herein referred to as "colored component removing operation (operation for removing the colored component)" in some cases). The place, at which the solution containing the catalyst is extracted, may be any place at which the solution contains the catalyst to be circulated. However, for example, it is preferable to extract a part of the outlet solution or liquid obtained at the outlet of the carbonation reactor. The extracting amount is appropriately to such an extent that the colored component is not concentrated in this process, because the solution or liquid is circulated again to the EC production process after removing the colored component. The extracting amount is 1/500 to 1/5 and preferably 1/100 to 1/10 of the outlet solution obtained at the outlet of the carbonation reactor.

[0022] As for the amount of addition of water to the extracted solution containing the catalyst, it is necessary to add an amount of water required to deposit the colored component. The amount of addition of water is not less than 20 times by weight, preferably not less than 50 times by weight, and most preferably not less than 60 times by weight with respect to the contained catalyst. As for the maximum amount, if a large amount of water is contained in the process, an extremely large amount of energy is finally required to remove water. Therefore, it is appropriate that the maximum amount is not more than 100 times by weight and preferably not more than 200 times by weight with respect to the amount of the contained catalyst.

[0023] The operation for recovering the catalyst and the

operation for removing the colored component can be also performed continuously for the solution containing the catalyst extracted as described above. At first, the catalyst is recovered as described above from the extracted solution containing the catalyst. The recovered catalyst may be used as it is, or the recovered catalyst may be dissolved, for example, in ethylene glycol to obtain a solution which may be used as the solution containing the catalyst. Water may be added thereto to remove the colored component as well. The amount of addition of water, which is adopted in this procedure, is also the same as or equivalent to the above.

[0024] As for the method for adding water, any special apparatus is not required when the catalyst concentration is thin or low. For example, a piping for water may be connected to the solution containing the catalyst to cause the mixing in the piping. On the other hand, when the catalyst concentration is, for example, 40% by weight which is high, the catalyst is temporarily deposited when water is added. Therefore, it is preferable to perform the operation in a dissolving vessel or tank equipped with an agitator.

The colored component is deposited after adding water. Therefore, the deposited colored component is separated and removed by means of any appropriate method. Specifically, the separating and removing method may be any method including, for example, the static separation, the filtration, and the adsorptive removal. In the case of the static separation, it is necessary to hold the solution or liquid for a period of time required to precipitate the colored component. A supernatant is recovered as the catalyst solution after statically placing the solution or liquid preferably for not less

than 0.5 hour and more preferably for not less than 1 hour. As for the apparatus to be used when the static separation is performed, for example, an apparatus may be used as a precipitation vessel or tank, wherein an ordinary vessel is provided with an inlet piping and an outlet piping which are installed at opposite positions to decrease the flow velocity at the inside.

[0025] In the case of the filtrating separation, the separation may be performed by using an ordinary filtration apparatus or strainer. However, the colored component is gradually aggregated or coagulated after the addition of water, and the filtration is performed with ease. Therefore, it is preferable that the filtration is performed after holding the solution or liquid preferably for not less than 5 minutes and more preferably for not less than 30 minutes, in view of the filtration performance of the colored component. As for the apparatus for the filtration, it is appropriate to use a commercially available ordinary filtration apparatus or strainer.

In the adsorptive separation, it is also allowable to use an adsorbent including, for example, ordinary activated carbon and zeolite. However, it is preferable to use a cottony material including, for example, glass wool, polypropylene wool, cotton, and metal wool, because of such a property possessed thereby that the colored component is physically adhered or adsorbed with ease. Specifically, as for the apparatus to be used, for example, the solution or liquid containing the catalyst added with water as described above is allowed to pass through an adsorption vessel or tank charged with glass wool, and thus the colored matters can be removed satisfactorily.

[0026] The period of time, for which the solution or liquid is allowed to pass, is not specifically limited. When the density of the absorbent is thin or low, it is necessary to allow the solution to flow slowly. However, when the absorbent is charged densely, the adsorption treatment can be performed in a short period of time. It is also allowable that a period of time is provided to aggregate the colored component before the supply to the adsorption vessel. However, the two effects are achieved by providing a period of time for the adsorption of about 15 minutes to 3 hours in order to simultaneously perform the two of the adsorption and the aggregation in the adsorption vessel. The solution containing the catalyst, which is obtained after removing the colored component, is circulated to the carbonation reaction of the EC production process. The position, at which the solution containing the catalyst is returned, may be any place provided that the catalyst is circulated at the place. The position includes, for example, the inlet of the carbonation reactor, the outlet of the carbonation reactor, and the catalyst separation step.

[0027] Ethylene carbonate, which is produced by the EC production process of the present invention, has no coloring, and it has a high purity. Therefore, ethylene carbonate is preferably usable as the raw material, for example, for the non-aqueous electrolyte solution (electrolytic solution). The term "no coloring" specifically refers to the fact that Hazen number is not more than 10. Ethylene carbonate having Hazen number of not more than 10 and a purity of not less than 99.999% and the non-aqueous electrolyte solution containing concerning ethylene carbonate are also included

in the present invention. The non-aqueous electrolyte solution of the present invention contains an electrolyte and a non-aqueous solvent for dissolving the same in the same manner as any ordinary non-aqueous electrolyte solution. The non-aqueous electrolyte solution of the present invention usually contains these components as main ingredients, which is produced in accordance with a method to be ordinarily employed.

[0028] (3) Method for producing ethylene glycol

Another aspect of the present invention resides in a method for producing ethylene glycol based on a process (referred to herein as "EG production process" in some cases) comprising the steps of obtaining a reaction solution containing ethylene carbonate and ethylene glycol by reacting carbon dioxide, ethylene oxide, and water in the presence of a catalyst and converting ethylene carbonate to ethylene glycol by further adding water to the obtained reaction solution (hydrolysis step), the method comprising extracting a solution containing the catalyst from the reaction solution, adding water to the extracted solution in an amount of not less than 20 times by weight an amount of the catalyst dissolved in the extracted solution to deposit undissolved matters, removing the deposited undissolved matters from the extracted solution and then circulating the resultant solution to the process. The colored component of ethylene carbonate, which is to be removed in the method for producing ethylene carbonate described above, causes the clog-up or blockade in the hydrolysis step of the method for producing ethylene glycol in another viewpoint. Therefore, when the colored component is removed in accordance with the same or equivalent method, it is

possible to produce ethylene glycol stably for a long term.

[0029] The step of obtaining a reaction solution containing ethylene carbonate and ethylene glycol by reacting carbon dioxide, ethylene oxide, and water in the presence of the catalyst in the method for producing ethylene glycol of the present invention is the same as or equivalent to the EC production process described above. The carbonation reaction solution is supplied to the hydrolysis step. However, a part of ethylene carbonate can be separated and purified therefrom in accordance with an appropriate method. In this procedure, the method for purifying ethylene carbonate is not limited to only the crystallization method described above. It is also possible to use, for example, a known distillation method. Of course, when the purification is performed in accordance with the crystallization method described above, it is possible to obtain ethylene carbonate which has no coloring and which has a high purity.

[0030] It is advantageous to perform the reaction at a high temperature in the hydrolysis step, in view of the reaction velocity. However, if the temperature is excessively high, it is feared that the quality of ethylene glycol may be deteriorated. Therefore, it is usually preferable to perform the reaction at 100 to 180°C. The reaction pressure is arbitrary within a range up to the boiling point of the solution or liquid. However, it is usually preferable to perform the reaction at a pressure from atmospheric pressure to 2.1 MPa. Further, it is also preferable to facilitate the hydrolysis by raising the reaction temperature and/or lowering the reaction pressure as the hydrolysis proceeds. Specifically, it is possible to use methods described, for example, in Japanese Patent Application

Laid-open Nos. 59-13741 and 2000-128814 in relation to, for example, the raw material and the amount of addition of water.

[0031] Ethylene glycol can be obtained in accordance with a known method from the preparation of ethylene glycol produced by the hydrolysis. Usually, water is separated by performing the distillation, preferably the distillation under reduced pressure to obtain crude ethylene glycol composed of, for example, ethylene glycol, diethylene glycol, other high boiling point components, and the carbonation catalyst. After that, in order to separate the catalyst from ethylene glycol, crude ethylene glycol is supplied to an evaporation apparatus. A greater part of ethylene glycol and parts of the high boiling point components are evaporated and recovered to obtain a residual liquid composed of, for example, the catalyst, remaining ethylene glycol, and the high boiling point components. The residual liquid is supplied as the "catalyst solution" to the carbonation reaction described above. The catalyst recovery step is also performed at a reduced pressure in order to facilitate the evaporation or vaporization of ethylene glycol and the high boiling point components. An apparatus provided with a reboiler is used as the evaporation apparatus, wherein the energy required for the evaporation is supplemented, and the evaporation amount is controlled.

[0032] Also in the EG production process of the present invention, the solution containing the catalyst is extracted from the reaction solution. Water is added in an amount which is not less than 20 times by weight an amount of the dissolved catalyst to remove deposited undissolved matters. After that, the solution is

circulated again to the process. In this procedure, the solution containing the catalyst may be any solution or liquid provided that the catalyst in the EG production process is contained. However, for example, the outlet solution obtained at the outlet of the carbonation reactor or the reaction solution of the hydrolysis step is preferably used.

[0033] Also in this EG production process, the catalyst recovery operation may be performed in order to avoid any further degradation of the catalyst in relation to the catalyst recovered in the catalyst recovery step, and the solution, which is obtained by dissolving the recovered catalyst, for example, in ethylene glycol, may be used as the solution containing the catalyst. Also in this procedure, the position, at which the circulation solution or liquid is returned, includes, for example, the carbonation reactor and the hydrolysis reactor.

[0034] Example 1: Production of Ethylene Carbonate

(1) Carbonation reaction

A carbonation reaction solution containing ethylene carbonate and ethylene glycol (EG) was obtained by supplying 5 parts by weight/Hr of tributylmethylphosphonium iodide, 0.8 part by weight/Hr of potassium carbonate, and 78 parts by weight/Hr of raw material ethylene oxide aqueous solution (60% by weight) to a first reactor at 100°C having a residence time of 1 hour pressurized with carbon dioxide at 2.0 MPa. The obtained reaction solution was extracted at 3 parts by weight/Hr, to which water was added in an amount that was 60 times by weight an amount of the contained catalyst. The solution

was allowed to pass through an adsorption vessel charged with wool made of polypropylene (produced by DCM Japan Co., Ltd.) at SV = 1. The catalyst solution allowed to pass therethrough had a pale yellow color. The solution was used and circulated to the carbonation reactor.

(2) Purification of ethylene carbonate

The operation was continued for 1 month, and then ethylene carbonate was crystallized and purified from the carbonation reaction solution in accordance with a method described in WO 2007/108213. Specifically, a vertical type melting purification apparatus described in Japanese Patent Application Laid-open No. 6-91103 was used as a crystallization apparatus. The purification apparatus is provided with an agitator. An agitation shaft having a horizontal agitation rod was used as an agitation impeller equipped to the agitator. A slit-shaped inspection hole (observation hole or viewing window), which was provided in order to confirm the accumulation or sedimentation of crystals, was installed on a side surface of the crystallization apparatus to be used.

[0035] A part of the reaction solution obtained in the carbonation reaction was cooled to 17°C by means of a crystallizing apparatus equipped with a cooling jacket as described in Japanese Patent Application Laid-open No. 6-91103. A slurry containing crystals of ethylene glycol was prepared, which was supplied from a crystal supply tube of the crystallization apparatus described above. The crystals were sedimented in the crystallization apparatus. An excessive amount of mother liquor was recovered as a overflow liquid from an upper portion of the crystallizer, which was circulated to

the hydrolysis reactor.

[0036] The crystals were sedimented, and the crystals were progressively accumulated at the tower bottom. The crystals were heated by a heater to melt the crystals, and a melted solution was formed. The melted solution was initially moved upwardly while being brought in contact in countercurrent with the crystals sedimented as the reflux liquid, and the melted solution was extracted from an upper extracting tube. The solution was returned to the hydrolysis reaction via the crystallizing apparatus.

Ethylene glycol was not extracted from a product extracting tube at this point in time, and an accumulated layer of crystals was formed on the melted solution. The thickness of the accumulated layer of crystals was observed from the inspection hole, and the extracting amount from the product extracting tube was adjusted so that the thickness of the accumulated layer of crystals had a height of 95% of the crystallization apparatus.

[0037] The operation was continued for 3 days, and the quality of the ethylene carbonate product was evaluated by using a gas chromatograph and a Karl Fischer moisture meter. As a result, the ethylene glycol concentration in the product was 1 ppm, and the moisture content or water content was 2 ppm. In other words, the purity of the ethylene carbonate product was not less than 99.999%. As for the hue, Hazen number (APHA) was not more than 10.

[0038]

Comparative Example 1

Ethylene carbonate was produced in the same manner as in Example 1 except that the step of extracting the reaction solution obtained

from the carbonation reaction and adding water to remove deposited matters was not performed. An ethylene carbonate product, which was obtained after the operation for 1 year, had an ethylene glycol concentration and a moisture content which were unchanged as compared with Example 1. However, the hue was slightly reddish, and the deepness of color was represented by Hazen number (APHA) of about 25.

[0039]

Examples 2 to 6

The step of removing deposited undissolved matters was performed in the same manner as in Example 1 except that the amount of water to be added and the method for removing undissolved matters were changed in the step of extracting the reaction solution obtained from the carbonation reaction and adding water to remove deposited matters. Obtained results are shown in Table 1. As clarified from Table 1, any coloring was not observed for the solution obtained after removing undissolved matters or components from the solution containing the catalyst when the amount of water added to the solution containing the catalyst was 20 times by weight the catalyst amount.

[0040]

Table 1

	Amount of addition of water (times by weight/catalyst amount)	Method for removing undissolved matters or components	State after removal of undissolved matters
Example 2	200	static placement for 3 hours decantation of supernatant	no coloring
Example 3	80	filtration with 5C filter paper	no coloring
Example 4	60	flow at SV = 8 through adsorption vessel charged with wool made of polypropylene	no coloring
Example 5	60	flow at SV = 8 through adsorption vessel charged with glass wool	no coloring
Example 6	40	filtration with 5C filter paper	substantially no coloring
Comp.Ex. 2	10	filtration with 5C filter paper	coloring in extent equivalent to that before filtration

[0041]

Comparative Example 2

The step of removing deposited undissolved matters or components was performed in the same manner as in Example 1 except that the amount of water to be added was 10 times by weight the catalyst amount and the method for removing undissolved matters was changed to the filtration in the step of extracting the reaction solution obtained from the carbonation reaction and adding water to remove deposited matters. Obtained results are shown in Table 1. As clarified from Table 1, the solution, which was obtained after removing the undissolved matters from the solution containing the catalyst, was unchanged from that before the filtration, and the colored component was not removed when the amount of water added to the solution containing the catalyst was 10 times by weight the catalyst amount.

[0042]

Example 7: Method for Producing Ethylene Glycol

The procedure was carried out in the same manner as in Example 1 until arrival at the carbonation reaction. The carbonation reaction solution was transferred to a second reactor in which the residence time was 2 hours and the pressure was 0.5 MPa at 150°C, and contained ethylene carbonate was hydrolyzed to obtain 66.5 parts by weight/Hr of an aqueous solution of ethylene glycol containing the catalyst. In this procedure, a part of the carbonation reaction solution was extracted by 3 parts by weight/Hr from the first reactor. An amount of water, which was 60 times by weight the amount of the catalyst contained in the solution, was added. The solution was allowed to pass through an adsorption vessel which was charged with wool made of polypropylene (produced by DCM Japan Co., Ltd.) at SV = 1. The solution allowed to pass therethrough was used and circulated to the carbonation reaction step.

[0043] The obtained reaction solution of the hydrolysis reaction was distilled, for example, by means of the distillation under reduced pressure of 80 torr at 140°C at the tower bottom to obtain a dehydrated solution from the tower bottom. Further, a greater part of ethylene glycol was evaporated therefrom by means of a reduced pressure evaporator operated at 140°C and 60 torr. A catalyst solution, in which the catalyst was concentrated, was recovered by 13 parts by weight/Hr from a bottom portion of the evaporator. The recovered catalyst solution was used and circulated as the catalyst to the first reactor. The catalyst solution had a color of vinegar upon the start of the operation, wherein any great change was not

observed in relation to the color of the catalyst solution after the continuous operation performed for 1 year. Any clog-up or any blockade was not caused in the control valve disposed at the outlet of the hydrolysis reactor, and the operation was successfully performed stably.

[0044]

Comparative Example 3

The operation was performed for 1 year in the same manner as in Example 7 except that the step of extracting the carbonation reaction solution to add water thereto and circulating the solution after removing deposited undissolved components was not performed. The catalyst solution had a color of vinegar upon the start of the operation, wherein the color of the catalyst solution was changed to a wine color after the continuous operation performed for 1 year. The clog-up or blockade was caused in the control valve disposed at the outlet of the hydrolysis reactor, and it was difficult to perform any stable operation.

[0045]

Example 8

The procedure was carried out in the same manner as in Example 7 until arrival at the hydrolysis reaction. The outlet solution was extracted from the hydrolysis reactor, to which water was added in an amount of 60 times by weight the amount of the catalyst contained in the solution, and then deposited undissolved components were filtrated with 5C filter paper. As a result, the turbidity was removed, and the catalyst solution having no coloring was successfully recovered.

Example 9

The procedure was carried out in the same manner as in Example 7 until a greater part of ethylene glycol was evaporated from the hydrolysis reaction solution and the catalyst solution, in which the catalyst was concentrated, was recovered by 13 parts by weight/Hr from the bottom portion of the evaporator. An amount of water, which was 180 times by weight the amount of the catalyst contained in the obtained catalyst solution, was added. As a result, the solution, which originally had a wine color, was turbid. Deposited undissolved components were filtrated with 5C filter paper. As a result, the turbidity was removed, and the catalyst solution having no coloring was successfully recovered. The precipitate, which was adhered to the filter paper, was washed with water, and then the precipitate was washed with methanol. As a result, methanol had a dark wine color, and the colored component contained in the catalyst solution was separated.

CLAIMS

1. A method for producing ethylene carbonate comprising obtaining a reaction solution containing ethylene carbonate by reacting carbon dioxide and ethylene oxide in the presence of a catalyst and purifying ethylene carbonate by means of crystallization, the method comprising extracting a solution containing the catalyst from the reaction solution, adding water to the extracted solution in an amount of not less than 20 times by weight an amount of the catalyst dissolved in the extracted solution to deposit undissolved matters, removing the deposited undissolved matters from the extracted solution, and then circulating the solution containing the catalyst from which the undissolved matter has been removed to the reaction solution.

2. The method according to claim 1, wherein the solution containing the catalyst is a part of an outlet solution obtained from a reactor for reacting carbon dioxide and ethylene oxide to produce ethylene carbonate.

3. A method for producing ethylene glycol comprising obtaining a reaction solution containing ethylene carbonate and ethylene glycol by reacting carbon dioxide, ethylene oxide, and water in the presence of a catalyst, and converting ethylene carbonate to ethylene glycol by further adding water to the obtained reaction solution, the method comprising extracting

a solution containing the catalyst from the reaction solution, adding water to the extracted solution in an amount of not less than 20 times by weight an amount of the catalyst dissolved in the extracted solution to deposit undissolved matters, removing the deposited undissolved matters from the extracted solution, and then circulating the solution containing the catalyst from which the undissolved matter has been removed to the reaction solution.

4. The method according to claim 3, wherein the solution containing the catalyst is a part of an outlet solution obtained from a reactor for reacting carbon dioxide, ethylene oxide, and water to produce ethylene carbonate and ethylene glycol and/or a part of an outlet solution obtained from a reactor for converting ethylene carbonate to ethylene glycol by adding water to the obtained reaction solution.

5. The method according to claim 1 or 2, wherein the undissolved matters are removed by means of static separation, filtrating separation, or adsorptive removal with an adsorptive substance.

6. The method according to claim 3 or 4, wherein the undissolved matters are removed by means of static separation, filtrating separation, or adsorptive removal with an adsorptive substance.

7. The method according to claim 1, 2 or 5, wherein the catalyst is quaternary phosphonium iodide or bromide.

8. The method according to claim 3, 4 or 6, wherein the catalyst is quaternary phosphonium iodide or bromide.