

DESCRIPTION

PROCESS FOR PRODUCING ALKYLENE DERIVATIVE AND METHOD FOR
REGENERATING CATALYST FOR THE PRODUCTION OF ALKYLENE
5 DERIVATIVE

TECHNICAL FIELD

The present invention relates to a process for producing an alkylene derivative such as an alkylene
10 glycol or an alkylene carbonate. Particularly, it relates to a process for producing an alkylene glycol such as ethylene glycol, which comprises reacting an alkylene oxide such as ethylene oxide, with water in the presence of carbon dioxide by means of a quaternary
15 phosphonium iodide and/or bromide catalyst, or a process for producing ethylene carbonate or the like, which comprises reacting an alkylene oxide with carbon dioxide. Especially, it relates to a method for efficiently recovering the quaternary phosphonium iodide and/or
20 bromide catalyst from this reaction system and recycling it for use.

In the present invention, an alkylene glycol means an alkylene glycol having from about 2 to 10 carbon atoms such as ethylene glycol or propylene glycol, and an
25 alkylene carbonate means an alkylene carbonate having from about 2 to 10 carbon atoms, such as ethylene carbonate or propylene carbonate.

BACKGROUND ART

Ethylene glycol is produced in a large scale by reacting ethylene oxide directly with water for hydrolysis. However, in this method, in order to
5 suppress formation of a byproduct such as diethylene glycol or triethylene glycol during the hydrolysis, it is required to use water in large excess over the stoichiometrical amount to ethylene oxide. Accordingly, it is necessary to remove the large excess amount of
10 water by distillation of the formed ethylene glycol aqueous solution, and there is a problem that a large amount of energy is required to obtain purified ethylene glycol.

As a method to solve such a problem, a method has
15 been proposed wherein ethylene oxide is reacted with water in the presence of carbon dioxide, to produce ethylene glycol. This reaction is a two step reaction wherein ethylene carbonate is formed by a reaction of ethylene oxide with carbon dioxide, and the ethylene
20 carbonate is hydrolyzed. In this two step reaction, water is present in the reaction system, whereby the reaction may proceed even in the same reactor, but in order to complete the reaction of the second step, a further reactor may be provided for the later step. In
25 the hydrolysis of ethylene carbonate, diethylene glycol or triethylene glycol will not substantially be formed as a byproduct, and accordingly, the hydrolysis can be

carried out with water in an amount slightly in excess of the stoichiometrical amount, whereby the cost required for removing water from the formed ethylene glycol aqueous solution can be substantially reduced. Further, carbon dioxide will be formed by the hydrolysis of ethylene carbonate formed by the reaction of ethylene oxide with carbon dioxide, and such carbon dioxide may be recycled for reuse.

Further, in this method, it is also possible to produce ethylene carbonate by suppressing the formation of ethylene glycol by reducing the amount of water in the starting material by lowering the temperature as a reaction condition.

Thus, various types of catalysts have been proposed for the production of ethylene glycol and/or ethylene carbonate from ethylene oxide. One of preferred catalysts is an organic phosphonium salt, and particularly preferred is a quaternary phosphonium iodide or bromide (JP-B-55-47617). Further, as a co-catalyst, an alkali metal carbonate may be used in combination with such an organic phosphonium salt (JP-A-12-128814).

Whereas, ethylene oxide as raw material is produced by oxidation of ethylene, and in such a case, in order to improve the selectivity for the oxidation reaction, a chlorohydrocarbon such as ethyl chloride is supplied as a selectivity-adjusting agent to the reaction system (JP-A-2-104579).

As mentioned above, the method for producing ethylene glycol or ethylene carbonate by reacting ethylene oxide with water or carbon dioxide in the presence of carbon dioxide, is an industrially
5 advantageous method free from a problem of byproducts, but has a problem that the reaction efficiency deteriorates when the reaction is continued.

The present inventors have studied the cause for such deterioration of the reaction efficiency and as a
10 result, have found that it is the cause that the quaternary phosphonium iodide or bromide catalyst in the reaction system is converted to a chloride having a low catalytic activity. In fact, by the operation of the apparatus for about one year, about 20 wt% of the
15 quaternary phosphonium iodide or bromide catalyst in the reaction system was found to be converted to a quaternary phosphonium chloride.

The reason for the conversion of the quaternary phosphonium iodide or bromide to the quaternary
20 phosphonium chloride was considered to be such that a chlorine compound contained as an impurity in ethylene oxide as raw material would be introduced into the reaction system. Namely, as mentioned above, in the process for producing ethylene oxide, a chlorohydrocarbon
25 is supplied as a selectivity-adjusting agent to the reaction system in order to improve the selectivity for the reaction, and chlorine contained in this

chlorohydrocarbon remains as a chlorine compound in the product ethylene oxide even via a purification system, and such a chlorine compound is included in the process for producing ethylene glycol or ethylene carbonate. It is considered that by the chlorine compound introduced as included in the product ethylene oxide, the quaternary phosphonium iodide or bromide will be converted to the quaternary phosphonium chloride, although the details of such reaction mechanism are not clearly understood.

Accordingly, in the process for producing ethylene glycol or ethylene carbonate, it is necessary to separate and remove from the reaction system the quaternary phosphonium chloride having a low reactivity derived from the catalyst, so as to let only the highly active quaternary phosphonium iodide or bromide remain. However, heretofore, it has not been ascertained even that the decrease of the reaction efficiency with time is caused by the conversion with time to the chloride. Further, there has been no study made with respect to a method for separating the quaternary phosphonium chloride from the quaternary phosphonium iodide or bromide as the catalyst in the reaction system, or a method for converting the quaternary phosphonium chloride to the quaternary phosphonium iodide or bromide.

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DISCLOSURE OF THE INVENTION

It is an object of the present invention to solve

the above-mentioned conventional problems and to provide a process for producing an alkylene derivative, such as an alkylene glycol such as ethylene glycol, or an alkylene carbonate such as ethylene carbonate, which
5 comprises reacting an alkylene oxide such as ethylene oxide with water or carbon dioxide in the presence of carbon dioxide by means of a quaternary phosphonium iodide and/or bromide catalyst, wherein a quaternary phosphonium chloride formed in the reaction system is
10 efficiently removed, or such quaternary phosphonium chloride is converted to quaternary phosphonium iodide and/or bromide, which will be recycled to the reaction system for reuse, whereby the catalytic activities in the reaction system can be maintained at a high level, and
15 the reaction for forming the alkylene derivative can be efficiently carried out constantly over a long period of time.

The present invention provides the following:

- (1) A process for producing an alkylene derivative,
20 which comprises a reaction step of reacting an alkylene oxide with water in the presence of carbon dioxide by means of a quaternary phosphonium iodide or bromide catalyst to form an alkylene glycol, characterized in that from at least a part of the reaction solution and/or
25 the catalyst solution, the alkylene glycol is removed so that the molar ratio of the alkylene glycol to the catalyst becomes at most 20 times, followed by mixing

with water to recover the catalyst.

(2) The process according to the above (1), characterized in that the molar ratio of the alkylene glycol to the catalyst is made to be at most twice.

5 (3) The process according to the (1) or (2), characterized in that the operation temperature at the time of mixing with water to recover the catalyst is at most 30°C.

(4) The process according to any one of the above (1) to
10 (3), characterized in that the amount of water to be mixed is at least 0.1 time by weight, based on the catalyst to be recovered.

(5) The process according to any one of the above (1) to (4), characterized in that after mixing with water,
15 solid-liquid separation is carried out to separate the catalyst, which is recycled to the reaction step.

(6) The process according to the above (5), wherein the liquid separated by the solid-liquid separation is recycled and used as water for washing the catalyst.

20 (7) The process according to any one of the above (1) to (6), characterized in that the alkylene oxide is ethylene oxide.

(8) A method for regenerating a catalyst, characterized in that a mixture comprising a quaternary phosphonium
25 chloride and a quaternary phosphonium iodide and/or bromide, obtained from a reaction step of reacting an alkylene oxide containing a chlorinated compound as an

impurity, with water in the presence of carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst, to form an alkylene glycol, is mixed with an iodide and/or bromide to have the quaternary

5 phosphonium chloride converted to a quaternary phosphonium iodide and/or bromide, which is precipitated in water.

(9) A method for regenerating a catalyst, characterized in that a mixture comprising a quaternary phosphonium
10 chloride and a quaternary phosphonium iodide and/or bromide, obtained from the reaction step of reacting an alkylene oxide with carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst, to form an alkylene carbonate, is mixed with an
15 iodide and/or bromide to have the quaternary phosphonium chloride converted to a quaternary phosphonium iodide and/or bromide, which is precipitated in water.

(10) The method according to the above (8) or (9), characterized in that the mixture comprising a quaternary
20 phosphonium chloride and a quaternary phosphonium iodide and/or bromide, is a reaction solution withdrawn from the above reaction step, or a residue after distilling water and/or at least a part of the alkylene derivative as the desired product, from such a reaction solution.

25 (11) The method according to the above (8) or (9), characterized in that the mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide

and/or bromide, is an aqueous solution obtained by mixing the reaction solution withdrawn from the above reaction step or the residue after distilling off water and/or at least a part of the alkylene derivative as the desired
5 product from such a reaction solution, with water to let the catalyst precipitate as solid, and separating the precipitated catalyst.

(12) The method according to any one of the above (8) to (11), characterized in that the precipitated quaternary
10 phosphonium iodide and/or bromide is recovered and recycled to the above reaction step.

(13) A method for regenerating a catalyst, characterized in that an iodide and/or bromide is added to a mixture comprising a quaternary phosphonium chloride and a
15 quaternary phosphonium iodide and/or bromide, obtained from the reaction step of reacting an alkylene oxide containing a chlorinated compound as an impurity, with water in the presence of carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a
20 catalyst, to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride in an organic solvent, thereby to recover the quaternary phosphonium iodide and/or bromide.

(14) A method for regenerating a catalyst, characterized
25 in that an iodide and/or bromide is added to a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained

from the reaction step of reacting an alkylene oxide with carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst to form an alkylene carbonate, to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride
5 in an organic solvent thereby to recover the quaternary phosphonium iodide and/or bromide.

(15) The method according to the above (13) or (14), characterized in that the mixture comprising a quaternary
10 phosphonium chloride and a quaternary phosphonium iodide and/or bromide, is any one of the following (a) to (c):

(a) A liquid or solid obtained by adding water to the reaction solution withdrawn from the above reaction step to precipitate the catalyst and dehydrating an
15 aqueous solution after separating the precipitated catalyst,

(b) A liquid or solid obtained by adding water to a residue after distilling off water and/or at least a part of the alkylene derivative as the desired product from
20 the reaction solution withdrawn from the reaction step, to precipitate the catalyst as solid, and dehydrating an aqueous solution after separating the precipitated catalyst,

(c) A liquid obtained by dissolving the liquid or
25 solid obtained by the dehydration in (a) or (b), in an organic solvent.

(16) The method according to the above (13) or (14),

characterized in that the mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, is either one of the following (d) and (e):

5 (d) A liquid obtained by diluting the reaction solution withdrawn from the reaction step, with an organic solvent,

 (e) A residue after distilling off water and/or at least a part of the alkylene derivative as the desired
10 product from the reaction solution withdrawn from the above reaction step, or a liquid obtained by dissolving such a residue in an organic solvent.

(17) The method according to any one of the above (13) to (16), characterized in that the recovered quaternary
15 phosphonium iodide and/or bromide is recycled to the above reaction step.

(18) A process for producing an alkylene derivative, which comprises a reaction step of reacting an alkylene oxide and carbon dioxide by means of a quaternary
20 phosphonium iodide and/or bromide as a catalyst to form an alkylene carbonate, characterized in that an iodide and/or bromide is added to a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained from the
25 reaction step, to have the quaternary phosphonium chloride converted to a quaternary phosphonium iodide and/or bromide, which is precipitated in water, and

recovered and recycled to the reaction step.

- (19) A process for producing an alkylene derivative, which comprises a reaction step of reacting an alkylene oxide and carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst to form an alkylene carbonate, characterized in that an iodide and/or bromide is added to a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained from the reaction step, to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride in an organic solvent, whereby the quaternary phosphonium iodide and/or bromide is recovered and recycled to the reaction step.
- 15 In the present invention, when the reaction solution containing the catalyst in a high concentration and/or the catalyst solution, is mixed with water, the iodide or bromide will precipitate, while the chloride derived from the catalyst will remain as dissolved in the liquid.
- 20 Namely, each of the iodide, bromide and chloride is highly soluble in an alkylene glycol or an alkylene carbonate, but the iodide or bromide has a low solubility in water, while the chloride has a high solubility in water. By subjecting the precipitated quaternary phosphonium iodide or bromide to solid-liquid separation,
- 25 it is easily possible to separate and recover the catalyst.

In the present invention, the catalyst may be precipitated, for example, as follows.

① The reaction solution containing the catalyst and/or the catalyst solution, is mixed with water and then
5 cooled.

② From the reaction solution containing the catalyst and/or the catalyst solution, at least a part of the alkylene glycol, is removed, followed by mixing with water.

10 In such a case, cooling operation is not necessarily required. However, in order to lower the solubility of the catalyst, it is preferred to carry out the cooling.

The quaternary phosphonium iodide or bromide thus recovered, can be recycled to the reaction step for reuse.

15 On the other hand, in the separated liquid after recovery of the quaternary phosphonium iodide or bromide by solid-liquid separation, a quaternary phosphonium chloride as a chlorine salt, is contained. This quaternary phosphonium chloride may be converted to a
20 quaternary phosphonium iodide or bromide by e.g. ion exchange, and then recovered, or recycled in a solution state to the reaction step for reuse.

Further, in the present invention, by adding an iodide and/or bromide to a mixture comprising a
25 quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained from a reaction step of reacting an alkylene oxide with water or

carbon dioxide in the presence of carbon dioxide by means of a quaternary phosphonium iodide and/or bromide catalyst, it is possible to convert the quaternary phosphonium chloride in the mixture to an iodide and/or bromide. Thus, the already present quaternary phosphonium iodide and/or bromide, and the quaternary phosphonium iodide and/or bromide formed by the reaction of the quaternary phosphonium chloride with an iodide and/or bromide, can be precipitated in water and recovered as precipitates.

In the following, the mixture comprising the quaternary phosphonium chloride and the quaternary phosphonium iodide and/or bromide, to which the iodide and/or bromide is added to convert the quaternary phosphonium chloride to a quaternary phosphonium iodide and/or bromide, may sometimes be referred to as "the mixture to be treated". Further, in the following, the liquid flowing out from the reactor, or the liquid withdrawn from the reactor, may sometimes be referred to simply as "the reaction solution", and the liquid in which the catalyst is concentrated by separating water and the alkylene glycol or the alkylene carbonate from the reaction solution by distillation, may sometimes be referred to simply as "the catalyst solution".

The present invention may be applicable directly to the reaction solution containing the catalyst, withdrawn from the reaction step for an alkylene glycol or an

alkylene carbonate, as the mixture to be treated.

However, as another method, it may be applied to a liquid after precipitating and recovering a part of the catalyst by adding water to a liquid-form catalyst solution or a
5 solid-form residue after removing by distillation a part or all of the alkylene glycol or the alkylene carbonate as the solvent in the reaction solution (hereinafter, the recovery operation by precipitating a part of the catalyst by adding water to such a catalyst solution or a
10 solid-form residue, may sometimes be referred to as "the pre-recovery"). By such pre-recovery treatment, the concentration of the quaternary phosphonium chloride in the mixture to be treated, can be increased, and it is possible to increase the conversion to and the recovery
15 of the quaternary phosphonium iodide and/or bromide.

Namely, the quaternary phosphonium iodide and/or bromide has a lower solubility in water than the quaternary phosphonium chloride. Accordingly, by such addition of water, most of the quaternary phosphonium
20 iodide and/or bromide will be precipitated, while most of the quaternary phosphonium chloride will be dissolved in water. By such pre-recovery treatment, the concentration of the quaternary phosphonium chloride in the mixture to be treated can be increased, and it is possible to
25 increase the conversion to and the recovery of the quaternary phosphonium iodide and/or bromide.

Further, as another method, at the time of carrying

out the above-mentioned pre-recovery, instead of adding water to the catalyst solution or the solid-form residue, an aqueous solution having an iodide and/or bromide dissolved, may be used, whereby the recovery rate of the quaternary phosphonium iodide and/or bromide may be increased.

In either method, when an iodide and/or bromide is added to the quaternary phosphonium chloride dissolved in water, the quaternary phosphonium chloride is precipitated in the form of the iodide and/or bromide, and in the solution, the chloride corresponding to the added compound remains as dissolved. Accordingly, the precipitated product is subjected to solid-liquid separation, whereby the quaternary phosphonium chloride can easily be separated and recovered in the form of the quaternary phosphonium iodide and/or bromide.

The quaternary phosphonium iodide and/or bromide thus recovered may be recycled for use to the reaction step for the alkylene glycol or the alkylene carbonate.

Further, according to the present invention, by adding an iodide and/or bromide to a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained from such a reaction step or from the above recovery step, to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride in the organic solvent, it is possible to recover the quaternary

phosphonium iodide and/or bromide.

Namely, by adding an iodide and/or bromide to a mixture comprising the quaternary phosphonium chloride and the quaternary phosphonium iodide and/or bromide, 5 obtained from the reaction step of reacting an alkylene oxide with water or carbon dioxide in the presence of carbon dioxide by means of a quaternary phosphonium iodide and/or bromide catalyst to form an alkylene glycol or an alkylene carbonate, it is possible to have the 10 quaternary phosphonium chloride in such a mixture converted to a quaternary phosphonium iodide and/or bromide. On the other hand, by letting chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride having a low solubility in an 15 organic solvent, in the organic solvent and separating the precipitated inorganic chloride, it is possible to recover the quaternary phosphonium iodide and/or bromide dissolved in the organic solvent.

In the following, such an operation to let chlorine 20 derived from the quaternary phosphonium chloride precipitate as an inorganic chloride in an organic solvent may sometimes be referred to as "the operation to precipitate an inorganic chloride". Further, the mixture comprising a quaternary phosphonium chloride and a 25 quaternary phosphonium iodide and/or bromide, to which an iodide and/or bromide is to be added to let chlorine of the quaternary phosphonium chloride precipitate as an

inorganic chloride, may also be referred to as "the mixture to be treated".

The separated liquid after converting the quaternary phosphonium chloride to the iodide or bromide and letting
5 chlorine derived from the chloride precipitate as an inorganic chloride in the organic solvent and separating the inorganic chloride, contains the quaternary phosphonium iodide and/or bromide dissolved in the organic solvent. Accordingly, by removing the organic
10 solvent in the separated liquid by evaporation, the quaternary phosphonium iodide and/or bromide can be recovered in the form of a solid. The recovered quaternary phosphonium iodide and/or bromide may be washed with water, if desired, and then, it may be, as it
15 is or after being dissolved in a proper solvent, recycled for use in the reaction step for an alkylene glycol or an alkylene carbonate.

BEST MODE FOR CARRYING OUT THE INVENTION

20 Now, the practical mode of the process for producing an alkylene glycol of the present invention is described in detail.

In the following, the present invention is described mainly with respect to a case where it is applied to a
25 reaction to produce ethylene glycol from ethylene oxide by means of a quaternary phosphonium iodide catalyst, but the present invention is by no means restricted thereto.

For example, the present invention is suitably applicable also to the production of various alkylene glycols, such as the production of propylene glycol from propylene oxide.

5 Further, the present invention is likewise applicable to a case where a quaternary phosphonium bromide is employed as the catalyst, or to a case where a quaternary phosphonium iodide and a quaternary phosphonium bromide are used in combination as catalysts.

10 Further, as mentioned above, the present invention is also applicable to a reaction to produce an alkylene carbonate such as ethylene carbonate, in a manner similar to such a process for producing alkylene glycol by changing the reaction conditions to lower the reaction
15 temperature to suppress the production of an alkylene glycol such as ethylene glycol. Further, it can also be applied to a reaction wherein both the alkylene carbonate and the alkylene glycol are the desired products.

 Further, in the following, a method is also
20 exemplified wherein an iodide is added to the mixture to be treated, to have a quaternary phosphonium chloride converted to a quaternary phosphonium iodide for recovery. Instead of the iodide, a bromide may be added to have the quaternary phosphonium chloride converted to a quaternary
25 phosphonium bromide for recovery, or an iodide and a bromide may be added in combination to have the quaternary phosphonium chloride converted to a quaternary

phosphonium iodide and a quaternary phosphonium bromide, for recovery.

Further, in the following, a method may be exemplified wherein an inorganic iodide is added to the mixture to be treated to have a quaternary phosphonium chloride converted to a quaternary phosphonium iodide, and at the same time, chlorine derived from a quaternary phosphonium chloride is precipitated as an inorganic chloride. Instead of the iodide, a bromide may be added to have the quaternary phosphonium chloride converted to a quaternary phosphonium bromide, and at the same time to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride, or an iodide and a bromide may be added in combination to have the quaternary phosphonium chloride converted to a quaternary phosphonium iodide and a quaternary phosphonium bromide and at the same time to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride.

As quaternary phosphonium catalysts which may be used in the present invention, the compounds disclosed in JP-B-58-22448 may be mentioned. Typical ones may, for example, be triphenylmethylphosphonium iodide, triphenylpropylphosphonium iodide, triphenylbenzylphosphonium iodide and tributylmethylphosphonium iodide. Such a quaternary phosphonium iodide catalyst is preferably supplied to the

reaction system so that it will be from 0.001 to 0.05
time by mol to ethylene oxide. Further, when a
quaternary phosphonium bromide catalyst is to be employed,
a bromide catalyst corresponding to the above quaternary
5 phosphonium iodide catalyst may be employed, and its
suitable amount is equal to the quaternary phosphonium
iodide catalyst.

In the present invention, an alkali metal carbonate
may be coexistent as a co-catalyst in the reaction system,
10 whereby the efficiency for the formation of ethylene
glycol may be increased. To let the alkali metal
carbonate be coexistent in the reaction system, a
hydroxide, carbonate or bicarbonate of an alkali metal
such as sodium or potassium, preferably potassium, may be
15 added, and when any one of the alkali metal compounds is
added, it will be present in the form of a carbonate in
the reaction system. In this case, an alkali metal
carbonate, preferably potassium carbonate, is preferably
incorporated so that it will be from 0.01 to 1 in a molar
20 ratio to the quaternary phosphonium iodide.

The amount of water to ethylene oxide may be reduced
to the stoichiometrical amount or lower than that
depending upon the reaction system. However, it is
preferably used in an amount of from 1.0 to 10.0 times by
25 mol to ethylene oxide. Further, with carbon dioxide, a
sufficient effect can be obtained in an amount of at most
equimolar to ethylene oxide, and under a usual condition,

it is employed in an amount of from 0.1 to 5.0 mols per mol of ethylene oxide. However, such a ratio is not necessarily strictly limited.

The reaction temperature varies depending upon the type of the alkylene oxide, the type of the catalyst, the composition of the reaction solution at the initial stage of the reaction, etc., but, the reaction is usually carried out within a range of from 50 to 180°C. The pressure varies depending upon the amount of carbon dioxide, the reaction temperature, etc., and it may further vary depending upon the progress of the reaction, but it is carried out usually within a range of from 0.5 to 5.0 MPa.

The type of the reactor is not particularly limited, so long as it is one whereby the gas-liquid reaction can be smoothly carried out. Further, the number of reactors and the retention time, are selected so that the desired conversion can be attained. Further, in a case where ethylene glycol is to be produced, a reactor may be added as the case requires to hydrolyze ethylene carbonate in the reaction solution.

From the reaction solution discharged from the reactor, water and the majority of ethylene glycol are separated by distillation. The remained liquid (the catalyst solution) containing the catalyst will be recycled to the reactor so that the catalyst will be used again for the reaction.

MODE FOR EFFICIENTLY RECOVERING THE QUATERNARY
PHOSPHONIUM IODIDE OR BROMIDE CATALYST FROM THE REACTION
SYSTEM AND RECYCLING IT FOR REUSE

5 In a case where the catalyst is to be recovered from
the reaction solution discharged from the reactor, the
catalyst concentration is thin, and the catalyst can
hardly be precipitated, as it is, and accordingly, it is
preferred to remove water and ethylene glycol contained
10 in the reaction solution to increase the catalyst
concentration, followed by mixing (the catalyst after
removal of ethylene glycol) again with water.

 In a case where the catalyst solution is used for
recovery of the catalyst, it is possible to recover the
15 catalyst by mixing the solution as it is with water, but
it is preferred to further remove the contained ethylene
glycol by distillation, followed by mixing with water to
recover the catalyst, in order to increase the recovery
rate of the catalyst.

20 Namely, in this reaction, at least part of the
reaction solution or the catalyst solution is withdrawn
from such a reaction step, and water and the alkylene
glycol, or the alkylene glycol, is removed so that the
molar ratio of the alkylene glycol to the catalyst
25 contained in the solution be at most 20 times when the
molar ratio is higher than that, preferably at most twice,
followed by mixing with water again.

In a case where the molar ratio of the alkylene glycol to the catalyst contained in the solution is lower than 20 times by mol, water may simply be mixed to have the catalyst precipitated and recovered.

5 When the liquid withdrawn from the reaction step is to be mixed with water, there may be a case where cooling is required to let the quaternary phosphonium iodide precipitate. Namely, the solubility of the quaternary phosphonium iodide in water or ethylene glycol will be
10 smaller as the temperature is lower.

The reaction solution withdrawn from the reaction step is usually at a level of from 100 to 180°C. It is preferred to cool the reaction solution so that the temperature of the solution after being mixed with water
15 becomes at most 30°C, preferably at a level of from 0 to 20°C, whereby the quaternary phosphonium iodide can be precipitated more efficiently. Whether or not such cooling is required, is determined depending upon the temperature of the reaction solution and the temperature
20 and amount of water to be mixed.

Further, to ensure the precipitation, it is preferred not only to carry out the cooling but also to add or preliminarily incorporate seed crystals, whereby the effect for precipitation under a stabilized condition
25 will be large.

Further, if at least a part, preferably the majority, of the product ethylene glycol is removed from the liquid

withdrawn from the reaction step, for example, if ethylene glycol (which may contain water) is removed so that the catalyst concentration will be at least 40 wt%, followed by mixing such a liquid with water, the

5 quaternary phosphonium iodide can be precipitated without necessity to carry out cooling, but it is still preferred to cool it to a level of at most 40°C, whereby the precipitation can efficiently be carried out.

The amount of water to be mixed, varies depending

10 upon the amount of the quaternary phosphonium iodide in the reaction solution, the amount of ethylene glycol, the amount of the chloride, cooling or not cooling, the recovery efficiency of the desired quaternary phosphonium iodide, etc., but if the amount is too small, filtration

15 tends to be difficult, and the efficiency to dissolve the quaternary phosphonium chloride tends to deteriorate. On the other hand, if the amount is too large, the amount of the quaternary phosphonium iodide contained in the liquid phase after separating the quaternary phosphonium iodide,

20 tends to increase. Usually, the amount of water to be added in one treatment is suitably determined within a range of at least 0.1 time by weight, preferably from 0.1 to 5 times by weight, to the liquid to be treated.

The liquid phase after separated from the solid can

25 be used again as water for washing the reaction solution, the catalyst solution or the catalyst separated from ethylene glycol. In such a case, if it is used

repeatedly as water for washing, the concentration of the quaternary phosphonium chloride contained in the water for washing will increase, whereby the concentration of the quaternary phosphonium chloride contained in the
5 quaternary phosphonium iodide to be recovered, will increase, and accordingly, after it is used for washing from once to five times, it is replaced with fresh water for washing.

A method wherein washing of the reaction solution is
10 carried out a plurality of times to gradually change to water for washing having a low concentration of quaternary phosphonium chloride, may also be carried out without any problem.

In a specific embodiment of this operation, cooled
15 water or a slurry of quaternary phosphonium iodide is preliminarily put in a vessel, and the reaction solution or the catalyst solution and water are continuously or batch-wise supplied thereto, and the mixture thereby obtained is continuously or batch-wise withdrawn, whereby
20 it is possible to recover the precipitate contained therein, by filtration.

Further, in order to separate ethylene glycol from the reaction solution, an operation of separating ethylene glycol by distillation under reduced pressure,
25 may be carried out. Water may also be separated together with ethylene glycol.

The precipitate thus obtained by mixing the reaction

solution with water, is usually a highly active quaternary phosphonium iodide catalyst having an iodide content of at least 90 wt% and a chloride content of at most 10 wt% and can effectively be recycled to the
5 reaction step for reuse.

Further, the separated liquid after separating the precipitate of the quaternary phosphonium iodide, contains the chloride i.e. the quaternary phosphonium chloride. Such a quaternary phosphonium chloride can be
10 converted to a quaternary phosphonium iodide, for example, by a method wherein the separated liquid is subjected to dehalogenation treatment with an OH type anion exchange resin, followed by neutralization with hydrogen iodide, or chlorine ions are directly exchanged to iodine ions by
15 an anion exchange resin substituted by iodine. Thus, the catalyst can be regenerated, and the regenerated catalyst thus obtained may also be effectively recycled to the reaction step for reuse.

In an application of the present invention, a part
20 of the reaction solution may be continuously or intermittently withdrawn from the reactor which is continuously operated, followed by recovery of the quaternary phosphonium iodide catalyst, and the recovered quaternary phosphonium iodide catalyst may be recycled to
25 the reactor. In such a case, the amount of the reaction solution and/or the amount of the catalyst solution, to be withdrawn for the recovery of the quaternary

phosphonium iodide catalyst, is not particularly limited. However, in order to remove the chloride and to maintain the reaction efficiency at a high level within a range not to excessively increase the recovery cost of the catalyst, it is preferred to withdraw the reaction solution continuously or intermittently for treatment, when the weight ratio of the chloride to the iodide in the reactor becomes within a range of from 0.01 to 1.0. The amount of withdrawal is not particularly limited, but preferably about 0.1 to 100 wt%, based on the amount of the reaction solution or the amount of the catalyst solution.

EMBODIMENT IN WHICH THE QUATERNARY PHOSPHONIUM CHLORIDE IN THE REACTION SYSTEM IS CONVERTED TO A QUATERNARY PHOSPHONIUM IODIDE AND/OR BROMIDE, WHICH IS RECOVERED AND RECYCLED TO THE REACTION SYSTEM FOR REUSE

The ratio or composition of the quaternary phosphonium chloride and iodide contained in the mixture to be treated comprising the quaternary phosphonium chloride and iodide, according to the present invention, varies depending upon the ratio of chlorine to iodine in the process for producing ethylene glycol, the breeding position, or the subsequent treatment as mentioned below (e.g. the presence or absence of the pre-recovery operation). The existing ratio and concentrations of the quaternary phosphonium chloride and iodide in the mixture

to be treated, are not particularly limited. However, the higher the ratio of the chloride to the iodide and the concentration of the chloride, the better from the viewpoint of the efficiency of the recovery operation.

5 Namely, the quaternary phosphonium chloride to the quaternary phosphonium iodide in the mixture to be treated is preferably at least 1/20, more preferably at least 1/10, by molar ratio, and the concentration of the quaternary phosphonium chloride in the mixture to be
10 treated is preferably at least 0.1 wt%, particularly preferably at least 1 wt%.

As specific examples for application of the present invention, the following respective methods may be mentioned for each of the method for obtaining the
15 mixture to be treated and the method for adding the iodide. They will be sequentially described, but it should be understood that the present invention is by no means restricted to the following methods.

20 APPLICATION EXAMPLE I

As a liquid containing the catalyst, a part of the liquid in the process for producing ethylene glycol is withdrawn. So long as it is a liquid containing the catalyst present in the process, there is no particular
25 limitation as to the position at which it is withdrawn. As mentioned above, the reaction for forming ethylene glycol from ethylene oxide is a two step reaction

comprising a reaction of ethylene oxide with carbon dioxide to form ethylene carbonate, and the hydrolysis of the ethylene carbonate to form ethylene glycol.

Accordingly, in a case where this reaction is carried out
5 by reactors provided in two steps in series, the liquid from this production process may be withdrawn from either reactor or may be withdrawn from both reactors.

In a case where the liquid is withdrawn at the outlet of the reactor, in order to increase the recovery
10 rate of the quaternary phosphonium iodide in the later step, it is preferred that the concentrations of the quaternary phosphonium chloride and iodide in the mixture to be treated, are high. Accordingly, in such a case, it is preferred to distil off water, ethylene glycol or
15 ethylene carbonate as the solvent for concentration. The distillation may be carried out by a distillation column, but a simple evaporator may otherwise be used.

Preferably, the concentration is carried out until the concentration of the quaternary phosphonium iodide in the
20 mixture to be treated becomes at least 1/20 time by mol of the solvent. Taking the heat resistance of the quaternary phosphonium salt into consideration, it is preferred to carry out this concentration operation by distillation under reduced pressure, preferably at most
25 400 Torr (53.2 Pa), preferably at a temperature of from 60 to 210°C.

The highly concentrated catalyst solution obtained

by concentration of the reaction solution by distillation, contains a quaternary phosphonium iodide and a quaternary phosphonium chloride formed by chlorination of the quaternary phosphonium iodide in the process for
5 producing ethylene glycol. Here, the catalyst solution may be one having the reaction solution taken out of the process and concentrated, or may be a catalyst solution withdrawn from a distillation column for separating the catalyst solution from water, ethylene glycol and
10 ethylene carbonate, in the process.

As the iodide to be used for recovering the quaternary phosphonium iodide, any iodide may be used so long as it is an ionic compound which may be dissociated in water and which is ion exchangeable with the
15 quaternary phosphonium chloride, and it may be suitably selected by a person skilled in the art. However, from the viewpoint of the solubility, toxicity, price, etc., an alkali metal salt such as a sodium salt or a potassium salt, or hydroacid may, for example, be preferred.

20 The inorganic iodide may be any iodide so long as it is an ionic compound which can be dissociated in water and which can be ion exchanged with the quaternary phosphonium chloride. However, from the viewpoint of the solubility, toxicity and price, an alkali metal salt such
25 as a sodium salt or a potassium salt, is preferred.

The amount of the iodide to be added, may be at least equivalent to the quaternary phosphonium chloride

present in the mixture to be treated. A preferred range is from 0.5 to 10 mols, more preferably from 1 to 5 mols, per mol of the quaternary phosphonium chloride present in the mixture to be treated. If the iodide is added more
5 than necessary, the recovery rate may be increased, but the excess iodide will be loss.

The iodide may be added in the form of solid or an organic solvent solution or an aqueous solution. However, in an industrial operation, it is preferably a liquid
10 from the viewpoint of the handling, and accordingly, it is preferably added in the form of an organic solvent solution or an aqueous solution.

In the case of the aqueous solution, the amount of water may be an amount sufficient to dissolve the iodide, and such an amount depends on the iodide to be used. For
15 example, in a case where potassium iodide is to be used, the saturated solubility in water is 60%, and water may be added so that the potassium iodide concentration in the mixture to be treated will be at most this level.
20 Usually, it is added in the form of an aqueous solution having a concentration of from 1 to 60 wt%.

The apparatus for adding the iodide to the mixture to be treated may be a container of any form, but it is preferred to employ a vessel having a stirring device to
25 accelerate the ion exchange reaction.

By this operation, the quaternary phosphonium chloride present in the mixture to be treated will be

converted to a quaternary phosphonium iodide, which will be precipitated in water together with the quaternary phosphonium iodide already present in the mixture to be treated. The temperature for precipitation is preferably
5 a low temperature, whereby remaining of the quaternary phosphonium iodide in water will be less. The precipitation is preferably carried out at a temperature of from 0 to 30°C.

The precipitated quaternary phosphonium iodide will
10 be subjected to filtration for recovery. The method for the filtration is not particularly limited, and not only usual filtration by means of a filter, but also centrifugal separation may, for example, be used.

The quaternary phosphonium iodide recovered in the
15 form of a solid, may sometimes contains about 10 wt% of the quaternary phosphonium chloride and the added iodide. At such a concentration, it may be recycled to the reaction step for ethylene glycol, as it is. However, if necessary, it may be washed with water to increase the
20 purity of the quaternary phosphonium iodide, before recycling for reuse. Water after used for washing contains the quaternary phosphonium iodide, and may be used for next washing or may be reused as water to dissolve the above-mentioned iodide to be added to the
25 mixture to be treated.

The recovered quaternary phosphonium iodide may, for example, be dissolved in ethylene glycol and as such, may

be recycled to the reaction system.

In the forgoing, an embodiment was described wherein a quaternary phosphonium chloride is converted to a quaternary phosphonium iodide, which is recovered. This
5 operation can be carried out also in an organic solvent. In the following, an embodiment will be described wherein an operation to precipitate an inorganic chloride is carried out in an organic solvent, whereby a quaternary phosphonium chloride is converted to a quaternary
10 phosphonium iodide, which is recovered.

In the highly concentrated catalyst solution obtained, ethylene glycol and/or ethylene carbonate is present as a solvent. Accordingly, to such a catalyst solution, the inorganic chloride-precipitating operation
15 of the present invention may be applied, but it is also effective to add another organic solvent in which the solubility of the inorganic chloride formed by the addition of the iodide, is low. Further, it is preferred that ethylene glycol and/or ethylene carbonate in the
20 highly concentrated catalyst solution is further removed to obtain a solid containing substantially no solvent, which is re-dissolved in another organic solvent, whereby the solubility of the inorganic chloride may be further decreased so that the precipitation efficiency will be
25 improved.

As the organic solvent to be used here, it is preferred to have a high ability to dissolve the

quaternary phosphonium salt while it has a low ability to dissolve the inorganic chloride. As a preferred solvent, an aliphatic halogenated hydrocarbon, a ketone, an alcohol, a nitrile, an amide, a urea compound or a carbonate may, for example, be mentioned.

Among them, the alcohol may, for example, be ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 1,1-dimethylethanol, 1-pentanol, 2-pentanol, 3-pentanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 1,1-dimethyl-1-propanol, 1-hexanol, 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 4-methyl-2-pentanol, 1-heptanol, 2-heptanol, 3-heptanol, 4-heptanol, 1-octanol, 2-octanol, 2-ethyl-1-hexanol, 1-nonanol, 2-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 1,6-hexanediol, cyclopentanol, cyclohexanol, benzyl alcohol or phenethyl alcohol.

The aliphatic halogenated hydrocarbon may, for example, be methylene chloride, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, 1,3-dichloropropane, 1,2,3-trichloropropane, 1,4-dichlorobutane or 1,6-dichlorohexane.

The nitrile may, for example, be acetonitrile, propionitrile, butyronitrile, adiponitrile or benzonitrile. The amide may, for example, be dimethylformamide or dimethylacetamide. The urea compound may, for example, be tetramethylurea or 1,3-dimethylimidazolidin-2-on. The ketone may, for example,

be acetone, methyl ethyl ketone or methyl isopropyl ketone. The carbonate may, for example, be ethylene carbonate, propylene carbonate or butylene carbonate.

As the organic solvent, one of them may be used
5 alone, or two or more of them may be used in combination as a mixture. The amount of the organic solvent to be added, is not particularly limited, but it is usually from 1 to 10 times by weight to the sum of the quaternary phosphonium chloride and iodide in the mixture to be
10 treated.

For example, sodium iodide is soluble in acetone very well, and such is a good combination. Further, potassium iodide is soluble in ethylene glycol very well, and such a combination is also good. However, in this
15 case, it is not necessarily required that the iodide is completely soluble in the organic solvent. Even if the saturated soluble amount of the iodide is very small, after added to the mixture to be treated, the iodide will be consumed by the reaction with the quaternary
20 phosphonium chloride, and the dissolution will further proceed to supplement the consumption. Consequently, the amount beyond the solubility will be reacted to form an inorganic chloride. Required for the selection of the iodide and the organic solvent is that there is a
25 difference in the mol solubility to the organic solvent between the iodide and the inorganic chloride to be formed by the reaction of this iodide with the quaternary

phosphonium chloride. As such a combination, butanol or ethylene glycol to potassium iodide may be mentioned as an example.

The apparatus for adding the iodide to the mixture
5 to be treated may be a container of any form, but it is preferred to employ a vessel having a stirring device in order to accelerate the ion exchange reaction.

By this operation, the quaternary phosphonium of the quaternary phosphonium chloride present in the mixture to
10 be treated will be converted to a quaternary phosphonium iodide, while chlorine will be precipitated as an inorganic chloride. The precipitation temperature is not particularly limited and may be determined in view of the dependency of the inorganic chloride on the dissolution
15 temperature, the boiling point or viscosity of the organic solvent to be used, and the solubility of the quaternary phosphonium salt. Usually, the precipitation is carried out at a normal temperature of from 0 to 50°C. The reaction of the iodide with the quaternary
20 phosphonium chloride will swiftly proceed when the viscosity of the solvent is low. However, in a case where the solvent has a high viscosity, or the solubility of the iodide is low, it is preferred to prolong the mixing time. Preferably, the reaction will be completed
25 in from about 1 minute to 3 hours. By this operation, the quaternary phosphonium of the quaternary phosphonium chloride in the organic solvent will be converted to the

iodide at a conversion of at least 90%, and at the same time, an inorganic chloride will be precipitated.

The precipitated inorganic chloride is removed by filtration. The method for the filtration is not particularly limited, and not only filtration by means of a usual filter, but also centrifugal separation or the like may be applied.

In the filtrate after separation of the inorganic chloride by filtration, a quaternary phosphonium iodide as the catalyst is dissolved. Accordingly, by removing the organic solvent from this filtrate by evaporation, the quaternary phosphonium iodide and, when added in an excess amount, the iodide, will be recovered in the form of a solid. Removal of the organic solvent may be carried out by a usual evaporator. Such removal of the organic solvent by evaporation is preferably carried out at a temperature of at most 200°C, if necessary, under reduced pressure, taking the heat resistance of the recovered quaternary phosphonium iodide into consideration, as mentioned above.

The purity of the quaternary phosphonium iodide thus recovered is at a level of at least 90% excluding the iodide added in an excess amount and the remaining solvent, and therefore, it can be recycled to the reaction step for reuse, as it is or as dissolved in a suitable solvent such as ethylene glycol. However, preferably, the recovered solid is washed with water to

remove the remaining iodide and the solvent, before being recycled to the reaction step for reuse. For such washing with water, washing water may be added to the recovered solid to form a slurry, which may be subjected to filtration or centrifugal separation. In such a case, the amount of washing water to be added is preferably made to be at most twice by weight to the recovered solid, taking the dissolution loss in the washing water into consideration.

As another method for removing the inorganic chloride in the above process, it is possible that without subjecting the inorganic chloride to filtration, removal of the solvent is carried out by a similar operation, and then, the above-mentioned washing with water is carried out to have the inorganic compound dissolved in water and removed.

The following process may be mentioned as another embodiment of the present invention.

APPLICATION EXAMPLE II

In Application Example I, a pre-recovery is carried out wherein water is added to and mixed with a highly concentrated catalyst solution wherein the concentration of a quaternary phosphonium iodide is at least 1/20 time by mol to ethylene glycol or which is concentrated to such a concentration, followed by cooling to have the quaternary phosphonium iodide selectively precipitated

and recovered. Here, the amount of water to be added is optional, but if it is too small, no adequate precipitation effect can be obtained, and therefore it is necessary to add at least 0.1 time by weight of the dissolved quaternary phosphonium iodide. The upper limit of the amount of water to be added, is not particularly limited, but in order not to increase the treating volume excessively, the amount is preferably adjusted to be at most about 5 times by weight to the dissolved quaternary phosphonium iodide. The temperature for this precipitation operation is preferably low, whereby the remaining amount of the quaternary phosphonium iodide in water will be small. The operation is preferably carried out at a temperature of from 0 to 30°C.

15 In the aqueous solution remaining after the recovery of the precipitated quaternary phosphonium iodide, an unprecipitated quaternary phosphonium iodide and a quaternary phosphonium chloride will be present. Such an aqueous solution remaining after the recovery of the quaternary phosphonium iodide may be used as the mixture to be treated, and it may be concentrated as the case requires, and then an iodide is added to carry out the conversion of the quaternary phosphonium chloride to a quaternary phosphonium iodide, and precipitation. It is preferred to carry out the concentration so that the quaternary phosphonium chloride concentration in the mixture to be treated prior to addition of the iodide

becomes to be at least 1 wt%, from the viewpoint of the conversion efficiency of the quaternary phosphonium chloride and the recovery efficiency of the quaternary phosphonium iodide.

5 The type of the iodide to be added, and the concentration and method for addition, the method for filtration of the precipitate, the subsequent treatment, etc. may be the same as in the above-mentioned Application Example I.

10 However, in this case, water is already present in the system, and the iodide may be added in a solid form, whereby the amount of water to be used will consequently be reduced, and the dissolution loss of the quaternary phosphonium iodide in waste water can be reduced.

15 Further, after carrying out the pre-recovery, the inorganic chloride precipitation operation can be carried out by using, as the mixture to be treated, one obtained by evaporating and removing preferably at least 90%, more preferably at least 99%, of water in the aqueous solution
20 containing the quaternary phosphonium chloride and iodide. Namely, such a mixture to be treated is dissolved in an organic solvent in an amount of from 1 to 10 times by weight to the sum of the quaternary phosphonium chloride and iodide in the mixture to be treated, and an iodide is
25 added thereto. The type of the iodide to be added, the concentration and method for addition, the method for filtration of the precipitate, the subsequent treatment,

etc., may be the same as in the above-described process of Application Example I.

Further, in this process, it is possible to add an aqueous iodide solution instead of water added to
5 precipitate the quaternary phosphonium iodide in the highly concentrated catalyst solution, and in such a case, addition of the iodide in the later stage will be unnecessary.

In either case, by removing the organic solvent from
10 the organic solvent solution after subjecting the precipitate of the inorganic chloride to solid-liquid separation, it is possible to further recover the quaternary phosphonium iodide, which may be re-used together with the previously recovered quaternary
15 phosphonium iodide.

The following process may be mentioned as a still another embodiment.

APPLICATION EXAMPLE III

20 In Application Example I, the highly concentrated catalyst solution wherein the concentration of the quaternary phosphonium iodide is at least 1/20 time to ethylene glycol or which is concentrated to such a concentration, is further concentrated, and at least 90%
25 of the solvent is distilled off. In such a case, the residue (the distillation residue) will solidify as it is cooled. The solidified residue may be washed with a

suitable amount of water, whereby the quaternary phosphonium chloride in the residue may be eluted to the water side and removed. Also in such a case, the temperature of water for washing is preferably low, as
5 the dissolution amount of the quaternary phosphonium iodide in the water for washing will be small. Washing is carried out preferably at a temperature of from 0 to 30°C.

The amount of the water to be used for washing is
10 not particularly limited. However, taking the washing efficiency and the loss of the quaternary phosphonium iodide in waste water into consideration, it is preferably from 0.5 to 10 times by weight to the solid residue to be washed. Water to be used for washing is
15 not required to be pure water, and it is possible to use recycled water within the process. Further, it may be repeatedly recycled for use. Especially, an aqueous solution containing the quaternary phosphonium iodide is preferred, since the dissolution loss of the quaternary
20 phosphonium iodide in water can thereby be reduced.

In water after washing, the eluted quaternary phosphonium chloride and a slight amount of dissolved quaternary phosphonium iodide will be present.

This may be used as a mixture to be treated, and as
25 mentioned above, it is concentrated as the case requires, and then an iodide is added to carry out conversion of the quaternary phosphonium chloride to the quaternary

phosphonium iodide, and precipitation. Also in this case, the concentration of the quaternary phosphonium chloride in the mixture to be treated before adding the iodide, is preferably at least 1 wt%, and the type of the iodide to be added, the concentration and method for addition, the method for filtration of the precipitate, the subsequent treatment, etc., may be the same as in the above-mentioned process of Application Example I.

Also in this case, water is already present in the system, and the iodide may be added in a solid form, whereby the amount of water to be used will be consequently reduced, and it is possible to reduce the dissolution loss of the quaternary phosphonium iodide in waste water.

Further, in the above-mentioned process wherein the washing operation is carried out, water after washing is used as a mixture to be treated, and an iodine is added thereto, the aqueous iodide solution may be used as water for washing, as a mode for carrying out the process as shortened. In this case, the concentration of the aqueous iodide solution to be used, may be a concentration such that the concentration of the iodine in water after washing will be the concentration in the above-mentioned added and mixed state.

The inorganic chloride precipitation operation can be carried out by using, as the mixture to be treated, one obtained by evaporating and removing preferably at

least 90%, more preferably at least 99%, of water in this aqueous solution containing the quaternary phosphonium chloride and iodide. Namely, this mixture to be treated is dissolved in an organic solvent in an amount of from 1
5 to 10 times by weight to the sum of the quaternary phosphonium chloride and iodide in the mixture to be treated, and an iodide is added thereto.

The type of the iodide to be added, the concentration and method for addition, the method for
10 filtration of the precipitate, the subsequent treatment, etc. may be the same as in the above-described process of Application Example I.

Further, also in this process, an aqueous iodide solution may be used instead of water for washing, and in
15 such a case, addition of the iodide at a later stage will be unnecessary.

In either case, by removing the organic solvent from the organic solvent solution after subjecting the precipitate of the inorganic chloride to solid-liquid
20 separation, it is possible to further recover the quaternary phosphonium iodide, which may be reused together with the previously recovered quaternary phosphonium iodide.

Further, a highly concentrated catalyst solution
25 wherein the concentration of the quaternary phosphonium iodide is at least 1/20 time to the ethylene glycol or which is concentrated to such a concentration, may be

further concentrated, and after distilling off at least 90% of the solvent, the solution may be maintained at a temperature of at least 90°C, whereby the liquid state can be maintained. Water is added thereto, followed by
5 cooling to from 0 to 40°C, whereby it is possible to precipitate the quaternary phosphonium iodide. Otherwise, the above-mentioned concentrated residue may be continuously supplied alone or together with water to the already existing cool water or slurry, to carry out
10 precipitation. Also in this case, in the aqueous solution remaining after separation and recovery of the precipitated quaternary phosphonium iodide, an unprecipitated quaternary phosphonium iodide and chloride will be present.

15 This may be used as a mixture to be treated, and as mentioned above, after concentrating it as the case requires, an iodide may be added to carry out conversion of the quaternary phosphonium chloride to the quaternary phosphonium iodide, and precipitation.

20 Also in this case, the concentration of the quaternary phosphonium chloride in the mixture to be treated prior to the addition of the iodide is preferably at least 1 wt%, and the type of the iodide to be added, the concentration and method for addition, the method for
25 filtration of the precipitate, the subsequent treatment, etc. may be the same as in the above-described process of Application Example I.

Thus, also in this case, water is already present in the system, and the iodide may be added in a solid form, whereby the amount of water to be used is consequently reduced, and the dissolution loss of the quaternary
5 phosphonium iodide in waste water can be reduced.

Further, as a mode to carry out the above process as shortened, it is also possible to use an aqueous iodide solution as heated, instead of water.

The inorganic chloride precipitation operation may
10 be carried out by using, as the mixture to be treated, one obtained by evaporating and removing preferably at least 90%, more preferably at least 99%, of water in this aqueous solution containing the quaternary phosphonium chloride and iodide. Namely, such a mixture to be
15 treated is dissolved in an organic solvent in an amount of from 1 to 10 times by weight to the sum of the quaternary phosphonium chloride and iodide in the mixture to be treated, and an iodide is added thereto.

The type of the iodide to be added, the
20 concentration and method for addition, the method for filtration of the precipitate, the subsequent treatment, etc. may be the same as in the above-described process of Application Example I.

Also in this process, it is possible to use an
25 aqueous iodide solution instead of water, and in such a case, addition of an iodide in the later stage will be unnecessary.

In all embodiments, it is also possible to apply the present invention to the quaternary phosphonium chloride and iodide still remaining in the separated liquid after solid-liquid separation of the inorganic chloride precipitated by adding an iodide. Namely, it is also possible to repeatedly carry out addition of the iodide and removal of the inorganic chloride until the desired recovery rate is reached.

In the application of the present invention, at least a part of the reaction solution and/or the catalyst solution is continuously or intermittently withdrawn from the reaction process which is continuously operated, and after carrying out concentration and/or pre-recovery as the case requires, conversion of the quaternary phosphonium chloride to a quaternary phosphonium iodide and recovery of the quaternary phosphonium iodide, are carried out, and the recovered quaternary phosphonium iodide catalyst may be recycled to the reactor. In such a case, the amount of the reaction solution and/or the catalyst solution withdrawn to recover the quaternary phosphonium iodide is not particularly limited. However, in order to maintain the reaction efficiency at a high level by removing the quaternary phosphonium chloride within a range not to excessively increase the cost for the recovery of the catalyst, it is preferred to continuously or intermittently withdraw the reaction solution and/or the catalyst solution for treatment when

the weight ratio of the quaternary phosphonium chloride to the iodide in the reactor becomes within a range of from 0.01 to 1.0. The amount for the withdrawal is not particularly limited, but it is preferably within a range of from about 0.1 to 100 wt%, based on the amount of the reaction solution or the catalyst solution in the respective system.

EXAMPLES

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such Examples.

EXAMPLE 1-1

Into a first reactor pressurized to 2.0 MPa by carbon dioxide for a retention time of 1 hour at 100°C, 5 parts by weight/hr of tributylmethylphosphonium iodide as a catalyst, 0.8 part by weight/hr of potassium carbonate, and 78 parts by weight/hr of the starting material ethylene oxide aqueous solution (60 wt%), were supplied to obtain a reaction solution comprising ethylene carbonate and ethylene glycol (EG). This solution was transferred in its entire amount to a second reactor for a retention time of 2 hours under a pressure of 0.5 MPa at a temperature of 150°C to have the contained ethylene carbonate hydrolyzed to obtain 66.5 parts by weight/hr of an aqueous solution of ethylene glycol, containing the

catalyst.

The obtained reaction solution was distilled by a vacuum distillation column having a bottom temperature of 140°C under a pressure of 11 kPa (80 mmHg) to obtain a dehydrated liquid from the bottom, and the liquid was further subjected to a vacuum evaporator operated at 140°C under a pressure of 8 kPa (60 mmHg) to evaporate the majority of ethylene glycol and to recover 13 parts by weight/hr of a catalyst solution having the catalyst concentrated, from the bottom of the evaporator. The recovered catalyst solution was recycled as a catalyst to the first reactor for reuse. The composition of the catalyst solution after the continuous operation for 1 year was as follows:

Composition of the Catalyst Solution

Ethylene glycol:	about 59 wt%
Iodide (quaternary phosphonium iodide):	about 33 wt%
Chloride (quaternary phosphonium chloride):	about 6 wt%
Potassium carbonate:	about 2 wt%

After the above composition was reached, the operation was changed so that a part of this catalyst solution was withdrawn at a rate of 0.02 part by weight/hr. The withdrawn catalyst solution (hereinafter referred to as "withdrawn liquid A") was supplied to a flush vessel, and under conditions of 3 Torr (400 Pa) and 128°C, about 93 wt% of ethylene glycol contained in the

liquid was removed.

The liquid after the removal of ethylene glycol (hereinafter referred to as "concentrated liquid A") was maintained at 95°C, and a 3 wt% potassium iodide aqueous solution was added, and the mixture was cooled to 20°C with stirring and mixing, whereupon it was left to stand for 1 hour. The potassium iodide added here was equimolar to the chloride in the concentrated liquid A, and the amount of water used was equal weight to the concentrated liquid A.

The precipitate was separated by a vacuum filter and analyzed, whereby the composition of this precipitate was as follows. This indicates that it was possible to efficiently separate 90 wt% of the iodide and chloride in the withdrawn liquid A, as the quaternary phosphonium iodide catalyst.

Composition of Precipitate

Water:	about 18 wt%
Ethylene glycol:	about 2 wt%
Iodide (quaternary phosphonium iodide):	about 80 wt%
Chloride (quaternary phosphonium chloride):	about 2 wt%
Potassium carbonate:	at most 1 wt%

This precipitate was dissolved in ethylene glycol and recycled to the reactor.

Thus, the operation was continued while recovery and recycling of the catalyst were carried out, whereby it

was possible to continue the operation efficiently without a problem of a decrease in the reaction efficiency in the process for production of ethylene glycol.

5 EXAMPLE 1-2

 In Example 1-1, instead of the potassium iodide aqueous solution, distilled water in the same amount as the concentrated liquid A, was added to the concentrated liquid A after separation and removal of ethylene glycol,
10 and a similar operation was carried out to have a solid precipitated.

 The precipitate was separated and analyzed, whereby it was confirmed that this precipitate contained 94 wt% of the iodide and about 13 wt% of the chloride in the
15 withdrawn liquid A, and it was possible to efficiently separate the quaternary phosphonium iodide catalyst from the chloride.

 In the liquid separated from the precipitate (hereinafter referred to as "separated liquid A"), about
20 6 wt% of the iodide and about 87 wt% of the chloride in the withdrawn liquid A were dissolved. To such a separated liquid A, potassium iodide in an amount of 1.2 times by mol to the chloride in the liquid was added in the form of a 50 wt% aqueous solution, and the mixture
25 was left to stand still at 20°C for 1 hour. The precipitate was separated and analyzed, whereby it was confirmed that in this precipitate, it was possible to

efficiently separate 50 wt% of the chloride in the withdrawn liquid A as the quaternary phosphonium iodide catalyst.

EXAMPLE 1-3

5 The separated liquid A obtained in Example 1-2 was distilled, and 50 wt% of water in the separated liquid A was distilled off for concentration. To such a concentrated liquid, potassium iodide in an amount of 1.2 times by mol to the chloride in the liquid was added in
10 the form of a 50 wt% aqueous solution, and the mixture was left to stand still at 20°C for 1 hour. The precipitate was separated and analyzed, whereby it was confirmed that in this precipitate, it was possible to efficiently separate about 75 wt% of the chloride in the
15 withdrawn liquid A as the quaternary phosphonium iodide catalyst.

EXAMPLE 2-1

Into a first reactor pressurized to 2.0 MPa by carbon dioxide for a retention time of 1 hour at 100°C, 5
20 parts by weight/hr of tributylmethylphosphonium iodide as a catalyst, 0.8 part by weight/hr of potassium carbonate, and 78 parts by weight/hr of a starting material ethylene oxide aqueous solution (60 wt%), were supplied to obtain a reaction solution comprising ethylene carbonate and
25 ethylene glycol (EG). This solution was in its entire amount transferred to a second reactor for a retention time of 2 hours, under a pressure of 0.5 MPa at a

temperature of 150°C to have the contained ethylene carbonate hydrolyzed to obtain 66.5 parts by weight/hr of an aqueous solution of ethylene glycol, containing the catalyst.

5 The obtained reaction solution was distilled by a vacuum distillation column at a bottom temperature of 140°C under a pressure of 11 kPa (80 mmHg) to obtain a dehydrated liquid from the bottom, and the liquid was further subjected to a vacuum evaporator operated at
10 140°C under a pressure of 8 kPa (60 mmHg) to evaporate the majority of ethylene glycol and to recover 13 parts by weight/hr of the catalyst solution having the catalyst concentrated, from the bottom of the evaporator. The recovered catalyst solution was recycled as a catalyst to
15 the first reactor for reuse. The composition of the catalyst solution after a continuous operation for 1 year, was as follows.

Composition of the Catalyst Solution

	Ethylene glycol:	about 59 wt%
20	Iodide (quaternary phosphonium iodide):	about 33 wt%
	Chloride (quaternary phosphonium chloride):	
		about 6 wt%
	Potassium carbonate:	about 2 wt%

After the above composition was reached, the
25 operation was changed so that a part of this catalyst solution was withdrawn at a rate of 0.02 part by weight/hr. The withdrawn catalyst solution (hereinafter

referred to as "withdrawn liquid A") was supplied to a flush vessel, and about 93 wt% of ethylene glycol contained in the liquid was removed under conditions of 3 Torr (400 Pa) and 128°C. The liquid after removal of
5 ethylene glycol (hereinafter referred to as "concentrated product A") was maintained at 95°C, and water in the same amount as the concentrated product A was added, and the mixture was cooled to 20°C with stirring and mixing, whereupon it was left to stand still for 1 hour.

10 The precipitate (hereinafter referred to as "precipitate A") was separated by a vacuum separator, and the obtained filtrate (hereinafter referred to as "filtrate A") was analyzed, whereby the composition of this filtrate A was as follows and was one containing
15 about 80 wt% of the chloride in the withdrawn liquid A.

Composition of Filtrate A

Water:	about 78 wt%
Ethylene glycol:	about 7 wt%
Iodide (quaternary phosphonium iodide):	about 1 wt%
20 Chloride (quaternary phosphonium chloride):	about 10 wt%
Potassium carbonate:	4 wt%

On the other hand, the above precipitate A was analyzed, whereby the composition of the precipitate A
25 was as follows, and this was one containing about 98 wt% of the iodide in the above withdrawn liquid A.

Composition of Precipitate A

Water: about 16 wt%
Ethylene glycol: about 1 wt%
Iodide (quaternary phosphonium iodide): about 80 wt%
Chloride (quaternary phosphonium chloride):

5 about 2 wt%
Potassium carbonate: at most 1 wt%

Water and ethylene glycol contained in the filtrate A were removed by means of an evaporator operated at 140°C. Along with the removal of water and ethylene glycol, the pressure was reduced, and finally, 5 Torr (660 Pa) was maintained for 30 minutes. By this operation, the amount of water and ethylene glycol contained in the distillation residue became at most 10 wt%. To the residue after thus removing water and ethylene glycol, acetone in the same amount by weight was added. Then, the obtained liquid was transferred to a vessel equipped with a stirrer, and sodium iodide in an amount of 1.2 times by mol to the contained chloride was added in the form of a solid, followed by stirring at room temperature for 1 hour. The precipitate formed by this inorganic chloride precipitation operation was separated by a vacuum filter and analyzed, whereby in this precipitate, sodium chloride corresponding to at least 98 wt% of the chloride in the filtrate A, was present. On the other hand, the filtrate obtained by this solid-liquid separation (hereinafter referred to as "filtrate B") was introduced into an evaporator operated

under 5 Torr (660 Pa) at 110°C, and substantially all amounts of acetone and ethylene glycol in the filtrate B were evaporated, and the obtained solid was mixed with water in the same amount by weight and washed, followed
5 by solid-liquid separation by a vacuum filter. The obtained solid (hereinafter referred to as "solid B") was analyzed and found to have the following composition.

Composition of Solid B

	Water:	about 17 wt%
10	Ethylene glycol:	at most 1 wt%
	Iodide (quaternary phosphonium iodide):	about 81 wt%
	Chloride (quaternary phosphonium chloride):	
		at most 1 wt%
	Sodium iodide:	about 1 wt%

15 One having this solid B and the above precipitate A combined, contains about 98 wt% of the iodide and the chloride in the withdrawn liquid A, as the quaternary phosphonium iodide, which was dissolved in ethylene glycol in the same amount by weight and recycled to the
20 reactor for reuse.

Thus, while recovery and recycling of the catalyst were carried out, the operation was continued, whereby it was possible to continue the operation efficiently without a problem of a decrease in the reaction
25 efficiency in the process for producing ethylene glycol.

EXAMPLE 2-2

In Example 2-1, to the concentrated product A after

separation and removal of ethylene glycol, n-butanol in the same amount by weight was added as an organic solvent for dissolution. This solution was transferred to a vessel equipped with a stirrer, and potassium iodide in the same molar amount as the chloride contained in the liquid, was added, followed by mixing at room temperature for 2 hours.

The precipitate was separated by a vacuum filter and analyzed, whereby in this precipitate, potassium chloride corresponding to at least 95 wt% of the chloride contained in the concentrated product A, was present.

On the other hand, the filtrate was introduced into an evaporator operated under 5 Torr (660 Pa) at 110°C, and substantially all amounts of butanol and ethylene glycol in the filtrate were evaporated. The obtained solid was mixed with water in the same amount by weight and washed, followed by solid-liquid separation by a vacuum filter. The obtained solid was analyzed and found to have the following composition, and it was one containing about 95 wt% of the iodide and the chloride in the withdrawn liquid A in the form of the quaternary phosphonium iodide.

Composition of Solid

Water:	about 18 wt%
Ethylene glycol:	2 wt%
Iodide (quaternary phosphonium iodide):	about 80 wt%
Chloride (quaternary phosphonium chloride):	

at most 1 wt%

Potassium iodide: at most about 1 wt%

This solid was dissolved in ethylene glycol in the same amount by weight and recycled to the reactor for
5 reuse.

Thus, while recovery and recycling of the catalyst were carried out, the operation was continued, whereby it was possible to continue the operation efficiently without a problem of a decrease in the reaction
10 efficiency in the process for producing ethylene glycol.

COMPARATIVE EXAMPLE 1

In Example 1-1, 100 g of the dehydrated reaction solution was withdrawn from the bottom of the vacuum distillation column. The ratio of ethylene glycol to the
15 catalyst contained therein was 87%. Water in the same amount by weight was added thereto, and the mixture was cooled to 0°C, but no precipitate was formed.

EXAMPLE 1-4

To the filtrate obtained in Example 1-2, potassium
20 iodide in an amount of 1 time by mol to the chloride in the liquid, was added in the form of a 50 wt% aqueous solution, and the mixture was left to stand still at 20°C for 1 hour. The precipitate was separated and analyzed. As a result, it was confirmed that in this precipitate,
25 it was possible to effectively separate about 87 wt% of the chloride in the filtrate, as the quaternary phosphonium iodide catalyst.

INDUSTRIAL APPLICABILITY

According to the present invention, in a process for producing an alkylene derivative, such as an alkylene glycol such as ethylene glycol, or an alkylene carbonate such as ethylene carbonate, which comprises reacting an alkylene oxide such as ethylene oxide with water or carbon dioxide, in the presence of carbon dioxide, by means of a quaternary phosphonium iodide and/or bromide catalyst, it is possible to efficiently recover the quaternary phosphonium iodide or bromide catalyst from the reaction system and to recycle it for use, or it is possible to convert the quaternary phosphonium chloride formed in the reaction system, efficiently to a quaternary phosphonium iodide and/or bromide, which can be recycled to the reaction system for reuse. Thus, it is possible to prevent accumulation in the system of the quaternary phosphonium chloride having a low catalytic activity and at the same time to convert it to a quaternary phosphonium iodide and/or bromide having a high catalytic activity and to recycle it for use, whereby it is possible to maintain the catalytic activity in the system at a high level and to carry out the reaction to form the alkylene derivative constantly and effectively over a long period of time.

25

The present invention is based on Japanese Patent Application No. 2003-031391 (filed on February 7, 2003),

Japanese Patent Application No. 2003-078178 (filed on March 20, 2003) and Japanese Patent Application No. 2003-088281 (filed on March 27, 2003), and their entireties are hereby included by reference.

CLAIMS

1. A process for producing an alkylene derivative, which comprises a reaction step of reacting an alkylene oxide with water in the presence of carbon dioxide by means of
5 a quaternary phosphonium iodide or bromide catalyst to form an alkylene glycol, characterized in that from at least a part of the reaction solution and/or the catalyst solution, the alkylene glycol is removed so that the molar ratio of the alkylene glycol to the catalyst
10 becomes at most 20 times, followed by mixing with water to recover the catalyst.
2. The process according to Claim 1, characterized in that the molar ratio of the alkylene glycol to the catalyst is made to be at most twice.
- 15 3. The process according to Claim 1 or 2, characterized in that the operation temperature at the time of mixing with water to recover the catalyst is at most 30°C.
4. The process according to any one of Claims 1 to 3, characterized in that the amount of water to be mixed is
20 at least 0.1 time by weight, based on the catalyst to be recovered.
5. The process according to any one of Claims 1 to 4, characterized in that after mixing with water, solid-liquid separation is carried out to separate the
25 catalyst, which is recycled to the reaction step.
6. The process according to Claim 5, wherein the liquid separated by the solid-liquid separation is recycled and

used as water for washing the catalyst.

7. The process according to any one of Claims 1 to 6, characterized in that the alkylene oxide is ethylene oxide.

5 8. A method for regenerating a catalyst, characterized in that a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained from a reaction step of reacting an alkylene oxide containing a chlorinated compound as an
10 impurity, with water in the presence of carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst, to form an alkylene glycol, is mixed with an iodide and/or bromide to have the quaternary phosphonium chloride converted to a quaternary
15 phosphonium iodide and/or bromide, which is precipitated in water.

9. A method for regenerating a catalyst, characterized in that a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or
20 bromide, obtained from the reaction step of reacting an alkylene oxide with carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst, to form an alkylene carbonate, is mixed with an iodide and/or bromide to have the quaternary phosphonium
25 chloride converted to a quaternary phosphonium iodide and/or bromide, which is precipitated in water.

10. The method according to Claim 8 or 9, characterized

in that the mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, is a reaction solution withdrawn from the above reaction step, or a residue after distilling water and/or
5 at least a part of the alkylene derivative as the desired product, from such a reaction solution.

11. The method according to Claim 8 or 9, characterized in that the mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or
10 bromide, is an aqueous solution obtained by mixing the reaction solution withdrawn from the above reaction step or the residue after distilling off water and/or at least a part of the alkylene derivative as the desired product from such a reaction solution, with water to let the
15 catalyst precipitate as solid, and separating the precipitated catalyst.

12. The method according to any one of Claims 8 to 11, characterized in that the precipitated quaternary phosphonium iodide and/or bromide is recovered and
20 recycled to the above reaction step.

13. A method for regenerating a catalyst, characterized in that an iodide and/or bromide is added to a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained
25 from the reaction step of reacting an alkylene oxide containing a chlorinated compound as an impurity, with water in the presence of carbon dioxide by means of a

quaternary phosphonium iodide and/or bromide as a catalyst, to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride in an organic solvent, thereby to recover the quaternary phosphonium iodide and/or bromide.

14. A method for regenerating a catalyst, characterized in that an iodide and/or bromide is added to a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained from the reaction step of reacting an alkylene oxide with carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst to form an alkylene carbonate, to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride in an organic solvent thereby to recover the quaternary phosphonium iodide and/or bromide.

15. The method according to Claim 13 or 14, characterized in that the mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, is any one of the following (a) to (c):

(a) A liquid or solid obtained by adding water to the reaction solution withdrawn from the above reaction step to precipitate the catalyst and dehydrating an aqueous solution after separating the precipitated catalyst,

(b) A liquid or solid obtained by adding water to a residue after distilling off water and/or at least a part of the alkylene derivative as the desired product from

the reaction solution withdrawn from the reaction step, to precipitate the catalyst as solid, and dehydrating an aqueous solution after separating the precipitated catalyst,

- 5 (c) A liquid obtained by dissolving the liquid or solid obtained by the dehydration in (a) or (b), in an organic solvent.

16. The method according to Claim 13 or 14, characterized in that the mixture comprising a quaternary phosphonium
10 chloride and a quaternary phosphonium iodide and/or bromide, is either one of the following (d) and (e):

(d) A liquid obtained by diluting the reaction solution withdrawn from the reaction step, with an organic solvent,

- 15 (e) A residue after distilling off water and/or at least a part of the alkylene derivative as the desired product from the reaction solution withdrawn from the above reaction step, or a liquid obtained by dissolving such a residue in an organic solvent.

20 17. The method according to any one of Claims 13 to 16, characterized in that the recovered quaternary phosphonium iodide and/or bromide is recycled to the above reaction step.

18. A process for producing an alkylene derivative, which
25 comprises a reaction step of reacting an alkylene oxide and carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst to form an alkylene

carbonate, characterized in that an iodide and/or bromide is added to a mixture comprising a quaternary phosphonium chloride and a quaternary phosphonium iodide and/or bromide, obtained from the reaction step, to have the
5 quaternary phosphonium chloride converted to a quaternary phosphonium iodide and/or bromide, which is precipitated in water, and recovered and recycled to the reaction step.

19. A process for producing an alkylene derivative, which
10 comprises a reaction step of reacting an alkylene oxide and carbon dioxide by means of a quaternary phosphonium iodide and/or bromide as a catalyst to form an alkylene carbonate, characterized in that an iodide and/or bromide is added to a mixture comprising a quaternary phosphonium
15 chloride and a quaternary phosphonium iodide and/or bromide, obtained from the reaction step, to let chlorine derived from the quaternary phosphonium chloride precipitate as an inorganic chloride in an organic solvent, whereby the quaternary phosphonium iodide and/or
20 bromide is recovered and recycled to the reaction step.