

Process for the preparation of cyclic organic carbonates

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(54) Title: PROCESS FOR THE PREPARATION OF CYCLIC ORGANIC CARBONATES

(57) Abstract: The present invention relates to process for the preparation of a cyclic organic carbonate comprising: reacting carbon monoxide and chlorine to form phosgene; reacting phosgene with a di- or polyhydric alcohol containing a vicinal diol moiety to form a reaction mixture comprising the cyclic organic carbonate and hydrogen chloride, which reaction proceeds via a chloroformate intermediate; and oxidizing the hydrogen chloride to chlorine and water, which chlorine is recycled to the phosgene synthesis reaction.



PROCESS FOR THE PREPARATION OF CYCLIC ORGANIC CARBONATES

The invention relates to a process for the preparation of cyclic organic carbonates via phosgene.

Processes to prepare organic carbonates by alcoholysis of phosgene are known. In these processes, phosgene is reacted with an alcohol under formation of the organic carbonate and hydrogen chloride (HCl) as the byproduct. The preparation of diaryl carbonates using phosgene is for instance known from EP 2371807 and EP 1112997. EP 2371807 discloses a process for the continuous preparation of diaryl carbonates from phosgene and at least one monophenol in the presence of catalysts. The hydrogen chloride formed in the reaction is converted by thermal oxidation into chlorine, with the chlorine being recirculated to the preparation of phosgene. More particularly, the described process comprises the steps of: (a) preparing phosgene by reaction of chlorine with carbon monoxide; (b) reacting the phosgene formed in step (a) with at least one monophenol in the presence of a catalyst to form at least one diaryl carbonate and hydrogen chloride; (c) isolating and working-up the diaryl carbonate formed in step (b); (d) isolating and optionally purifying the hydrogen chloride formed in step (b); (e) thermally oxidizing at least part of the hydrogen chloride from step (d) to chlorine by oxygen with formation of water; (f) recirculating at least part of the chlorine prepared in step (e) to the preparation of phosgene in step (a); wherein the thermal oxidation by oxygen in step (e) is carried out using one or more catalysts. EP 1112997 describes a process for producing diaryl carbonate comprising the steps of (a) subjecting an aromatic monohydroxy compound and phosgene to a condensation reaction at a temperature of 80 to 180°C in the presence of an aromatic nitrogen-containing heterocyclic catalyst to obtain a diaryl carbonate; (b) purifying the hydrogen chloride gas byproduced in the condensation reaction; (c) recovering chlorine from the purified hydrogen gas; (d) reacting recovered chlorine with carbon monoxide to obtain phosgene which can be used in the diaryl carbonate production step. Since phosgene is a highly poisonous compound, nowadays it is seldom used as a starting compound for the preparation of organic carbonates.

M.J. Climent *et al.* in *Journal of Catalysis*, 269 (2010) 140-149 describe the synthesis of glycerol carbonate by transesterification of ethylene carbonate with glycerol using a basic oxide (MgO, CaO) and mixed oxides (Al/Mg, Al/Li) derived from hydrotalcites as catalyst. The presence of a transesterification step in the synthesis route towards cyclic carbonates is undesired, however. This is due to the fact that this step involves an equilibrium, putting restrictions on the conversion towards the cyclic carbonate and the yield, reducing the economic attractiveness of the process. M.J. Climent *et al.* in this article furthermore describe the synthesis of glycerol carbonate by carbonylation of glycerol with urea. A drawback of that process is that NH₃ is produced as byproduct in stoichiometric amounts, which is especially undesired if the process is to be practised on an industrial scale.

It is an object of the present invention to provide a route towards cyclic organic carbonates wherein good to excellent yields are obtained and which is suitable for the synthesis of a wide variety of different types of cyclic organic carbonates. Furthermore, it is an object of the present invention to provide a process for the preparation of cyclic organic carbonates which is not very water-sensitive. In other words, it is an object to provide a process for which it is not necessary to remove water from the alcohols which are to be used as starting materials, as this is costly and time-consuming.

It has now been found that cyclic organic carbonates can advantageously be prepared via phosgene in a process wherein phosgene is formed in situ by chlorination of CO and wherein the HCl byproduct of the alcoholysis of phosgene is oxidized to chlorine, which in turn is recycled for use in the in situ preparation of phosgene. Additionally, the highly poisonous phosgene can advantageously be produced in an alcohol-rich environment, and will quickly react to less harmful substances, i.e. the intermediate chloroformate and the cyclic organic carbonate. In addition, a closed chlorine cycle is advantageously provided, and losses of chlorine will be minimal. Both factors will greatly diminish the environmental impact of the preparation of cyclic organic carbonates via phosgene. Furthermore, it was found that the chloroformate

intermediates according to the present invention are surprisingly stable enough towards hydrolysis. This means that diols or polyols which are used as starting materials in the process according to the present invention and which in crude form typically comprise small to considerable amounts of water, do not have to
5 be dried before use.

Accordingly, a process for the preparation of a cyclic organic carbonate is provided comprising:

reacting carbon monoxide and chlorine to form phosgene;

10 reacting phosgene with a di- or polyhydric alcohol containing a vicinal diol moiety to form a reaction mixture comprising the cyclic organic carbonate and hydrogen chloride, which reaction proceeds via a chloroformate intermediate; and

oxidizing the hydrogen chloride to chlorine and water, which chlorine is recycled to the phosgene synthesis reaction.

15

The cyclic organic carbonate preferably has the formula $R^1-O(C=O)O-R^2$, wherein R^1 and R^2 each independently are aliphatic and/or aromatic hydrocarbon moieties having a backbone of 1 to 12 carbon atoms, which R^1 and R^2 are the same or different and bonded to each other via at least a direct
20 bond forming a 5-membered ring containing the carbonate moiety. Most preferably, R^1 and R^2 each independently are the aliphatic hydrocarbon moieties as just described.

The R^1 and R^2 moieties may be linear or branched, saturated or unsaturated, substituted or unsubstituted, or may be part of an aliphatic and/or aromatic ring.
25 Suitable substituents are hydroxyl, halogen such as chlorine, secondary or tertiary amine, and/or alkoxy. The parts of the R^1 and R^2 moieties not taking part in the 5-membered ring may be part of or form a further aliphatic and/or aromatic ring structure. Most preferably, however, R^1 and R^2 are not part of nor comprise an aromatic ring. In one embodiment, the hydrocarbon moieties R^1
30 and R^2 each independently have a backbone of 1 to 8 carbon atoms, preferably 1 to 6 carbon atoms. In another embodiment, the R^1 and R^2 moieties are bonded to each other forming a 5-membered ring containing the carbonate moiety. In this embodiment, the R^1 and R^2 moieties further may together form a

phenyl or a cyclohexyl group. Most preferred, R¹ and R² are methyl and/or ethyl groups.

The water formed can conveniently be disposed off.

5 The overall process for the preparation of the cyclic organic carbonates as described herein encompasses three subprocesses, the chlorination of CO, the alcoholysis of phosgene, and the oxidation of HCl. These steps will be set out in more detail below.

A reactor as described herein may be a single reactor or may encompass a cascade of reactors.

10 Chlorination of CO

The reaction of CO and Cl₂ to phosgene (chlorination of CO) can be performed as known in the art, e.g. from *Encyclopedia of Polymer Science and Technology*, Vol. 3, pages 435-447, "Phosgene", K.L. Dunlap, John Wiley & Sons, Published online on October 22, 2001. This reaction typically takes place in the presence
15 of a suitable catalyst, at a temperature between 25 and 250°C and at atmospheric pressure or a pressure close to atmospheric, usually slightly higher than atmospheric. As a catalyst, an (activated) carbon catalyst of high adsorptive capacity (> 400 m²/g) may be employed, as is known to those skilled in the art.

20 The upper limit for the reaction temperature is about 250°C, to avoid an increased formation of side products. Preferably, the reaction is performed at a temperature between 25 and 250°C, more preferably at a temperature between 40 and 200°C. The reaction is highly exothermic, temperatures in excess of 400°C in the catalytic bed have been reported, and adequate heat removal is
25 important. Therefore, the reaction typically takes place in tubular heat exchangers with a granular activated carbon catalyst.

The temperature in the reactor may further be controlled by e.g. cooling, and the reactor may be flooded with a suitable liquid, aimed at dissipation of the

heat of reaction. A suitable liquid would be the cyclic organic carbonate itself. The feed rate of the gaseous components and liquid may be such that the peak temperature does not exceed 200°C.

To ensure complete conversion of CO, the reaction is preferably run at a molar
5 excess of Cl₂, more preferably at a slight molar excess (1.05-1.5) of Cl₂.

The starting compounds are as pure as possible to prevent unwanted reactions and the formation of side products. The chlorine and CO are preferably free of H₂O, H₂, and S. For instance, water will hydrolyze phosgene, and sulfur will form sulfur chlorides, which are highly undesirable. The presence of CO₂ in the
10 CO does not harm the reaction.

Alcoholysis of phosgene

The alcohol for use in the alcoholysis of phosgene provides the “organic” moiety of the cyclic organic carbonate. The alcohol is a dihydric or polyhydric (≥ 3 hydroxyl groups) alcohol containing a vicinal diol moiety. It may comprise a
15 primary, secondary or tertiary alcohol. The alcohol may be a single alcohol species or may be a mixture of at least two different alcohols.

The alcohol provides the R¹ and R² moieties of the organic carbonate. When using the dihydric or polyhydric (3 or more hydroxyl groups) alcohol according to the present invention, the organic carbonate will be a cyclic carbonate
20 wherein the R¹ and R² moieties are bonded to each other and the carbonate moiety of the cyclic carbonate is part of a 5-membered ring. In case of the use of a polyhydric alcohol, the hydroxyl groups above two are substituents on the R¹ and/or R² moieties.

As mentioned above, the dihydric or polyhydric alcohols according to the
25 invention contain a vicinal diol moiety. By the term “vicinal diol moiety” is meant that the alcohol comprises at least two hydroxyl groups in a vicinal position in relation to each other, i.e. the hydroxyl groups are attached to adjacent carbon atoms. Examples of such alcohols are C1-C6 alcohols such as 1,2,-butanediol, 2,3-butane-1,2-diol, 2-methyl-2,3-butane-1,2-diol, 2,3-dimethyl-2,3-butane-1,2-diol, 1,2-

propanediol, glycerol, catechol, and the like. Cyclic carbonates of interest are ethylene carbonate, propylene carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, and glycerol carbonate. As the skilled person will understand, it is also possible to use a precursor of a dihydric or polyhydric alcohol in the process according to the invention if the dihydric and the polyhydric alcohol, respectively, are generated under reaction conditions. Suitable examples of such compounds include esters of dihydric or polyhydric alcohols.

The reaction of phosgene and the alcohol to a cyclic organic carbonate (alcoholysis of phosgene) is a two-step reaction, and typically occurs via a chloroformate intermediate. The first step towards the chloroformate intermediate runs rather smoothly, whereas the second step towards the cyclic organic carbonate requires extra effort. The second step may be accelerated using an acid scavenger, such as a tertiary amine, e.g. triethylamine or pyridine, or a carbamate.

The reaction is performed in a reaction medium comprising the reaction components alcohol and phosgene and/or chloroformate. The reaction medium may further comprise an organic solvent, for instance functioning to dissipate heat of the reaction and/or to dissolve higher alcohols and products. Examples of suitable solvents are aromatic, optionally chlorinated, hydrocarbons, such as toluene, benzene. The reaction components alcohol and phosgene and/or chloroformate are generally employed in stoichiometric amounts, but the alcohol may, of course, also be used in excess.

The reaction temperature may depend on the alcohol used and the cyclic carbonate formed. Typically, the reaction is performed at a temperature in the range from about -20° to about 200°C, preferably in the range from about 5° to about 70°C, more preferably in the range from about 25° to about 50°C. For higher aliphatic alcohols, the reaction may be performed at a temperature above 60°C, whereas for a lower alcohol the temperature may be 0° to 10°C. Catalysts may be employed for further acceleration of the reaction, especially towards the end of the reaction. Suitable catalysts for instance are heterogeneous catalysts such as a high surface area (> 400 m²/g) activated carbon catalyst, optionally in combination with an acid scavenger.

The formed HCl and the cyclic organic carbonate can be recovered from the reaction mixture by separation methods known to a person skilled in the art, e.g., distillation, extraction, crystallization, membrane technologies, absorption, adsorption. The HCl may be separated from the reaction mixture prior to or after
5 separation of the cyclic organic carbonate. HCl may also be separated from the reaction medium during the alcoholysis reaction, to keep a high selectivity.

The alcoholysis of phosgene is commonly known to the skilled person. For instance, a process for the methanolysis of phosgene is described in US 2,787,631 or US 4,335,051. Example 1 of US 2,787,631 shows that the reaction
10 of phosgene with methanol between c. 40 and 70°C results in c. 95% yield of theoretical maximum, after 3 hrs. Reaction of phosgene with various lower (C3-C6) diols is described in JP61130288. Reaction of phosgene with glycerol is described in JP0609610. Reaction of phosgene with catechol is described in *Organic Syntheses, Coll.* Vol. 4, 788 (1963).

15 **Oxidation of HCl**

The HCl formed in the alcoholysis of phosgene is oxidized to chlorine. This oxidation may be done by any suitable process that is known to the skilled person.

A suitable process for oxidation of HCl is disclosed by Sumitomo in EP 1170250,
20 US 20100303710, US 20100296998, and in Sumitomo Tagaku, Vol. 2004-I. EP 1170250 discloses a process wherein the oxidation step of hydrogen chloride is done by contacting a gas containing the hydrogen chloride with a gas containing oxygen in the presence of a catalyst, and wherein the oxidation of hydrogen chloride is carried out in at least two reaction zones each comprising
25 a catalyst-packed layer, which are arranged in series, and a temperature in at least one of said reaction zones is controlled with a heat exchange system. The process preferably uses a RuO₂/TiO₂ catalyst.

The reaction is equilibrium limited: at higher temperatures, the equilibrium conversion of HCl drops from c. 92% at 250°C to less than 65% at 500°C.
30 Therefore, for this reaction to be economically viable, it preferably has to be

performed at a temperature below about 250°C, in particular at a temperature of 200 to 250°C.

The overall process as described herein may encompass the synthesis of phosgene by chlorination of CO and the synthesis of the cyclic organic carbonate by alcoholysis of phosgene in separate reactors as well as the
5 synthesis of phosgene in alcohol / chloroformate. The separate syntheses advantageously allow individual control of the reactions and the adjustment of the reaction conditions to optimal values for each synthesis reaction. The synthesis of phosgene in alcohol / chloroformate advantageously allows the
10 instantaneous reaction of formed phosgene with the alcohol.

For the separate syntheses, CO and Cl₂ are fed to a first reactor loaded with a suitable catalyst and reacted to yield phosgene, as described hereinabove. The temperature in the reactor can be controlled by e.g. cooling, and the reactor can be flooded with a suitable liquid, aimed at dissipation of the heat of reaction. A
15 suitable liquid would be the cyclic carbonate itself. The feed rate of the gaseous components and liquid is such that the peak temperature does not exceed 200°C.

The product stream is then fed to a second reactor in which the alcohol is added continuously, preferably in a slight molar excess compared to the amount
20 of phosgene entering the reactor. The alcohol will react with the phosgene, forming the corresponding chloroformate, and with the chloroformate yielding the cyclic organic carbonate. In a preferred mode of operation, the temperature is kept below the boiling point of the chloroformate, typically below about 70°C, more preferably below 50°C. Gaseous components are continuously removed
25 from the reaction mixture and partially condensed. Products such as HCl and unconverted Cl₂ are sent to the recovery section, as described herein, and condensable components are recycled to the reactor.

For the synthesis of phosgene in alcohol / chloroformate, a mixture of CO and Cl₂ is fed to a reactor filled with alcohol and loaded with a suitable catalyst, e.g.
30 a high surface area (> 400 m²/g) active carbon catalyst, optionally combined with a tertiary amine such as triethylamine or pyridine, or a carbamate.

Phosgene is generated, which essentially instantaneously reacts with the alcohol, yielding chloroformate and hydrogen chloride, which chloroformate reacts to the cyclic organic carbonate. The reactor configuration and the reaction conditions are chosen such that carbon monoxide is fully converted, and peak temperatures are kept below the boiling point of the chloroformate, typically below about 70°C. Also, gaseous components are continuously withdrawn from the reaction solution, with the condensable components thereof being recycled to the reactor and the gaseous components such as HCl and unconverted Cl₂ being fed to a recovery section as described below.

In one embodiment, the synthesis of the cyclic organic carbonate by alcoholysis of phosgene occurs in the reactor wherein the phosgene is synthesized. In another embodiment, after essentially full conversion of the phosgene to the chloroformate intermediate, the chloroformate and unreacted alcohol are fed to a second reactor. Additional alcohol is fed to this reactor, maintaining a slight molar excess of alcohol compared to the chloroformate, and the cyclic organic carbonate is formed.

After a sufficiently high degree of phosgene conversion is obtained, typically > 95%, the components are separated by technology known in the art, e.g., distillation, extraction, crystallization, membrane technologies, absorption, adsorption. An essentially pure cyclic organic carbonate product stream and a stream containing chloroformate and alcohol are obtained. The alcohol / chloroformate stream is recycled to the carbonate synthesis reactor and/or separated into alcohol and chloroformate, which would allow feeding of the chloroformate to the phosgene synthesis reactor.

A gaseous mixture comprising HCl and unconverted chlorine, which is continuously removed from the alcoholysis reaction mixture, is sent to a downstream chlorine recovery section. This recovery section comprises a reactor wherein pure oxygen is added to the gaseous mixture, essentially composed of HCl and low amounts of chlorine, and the mixture is contacted with a suitable catalyst, producing chlorine and water, as described herein. After subsequent condensation of the water produced, the gas stream is further dried, e.g. by molecular sieves or via membrane technology, and a c. 95% pure chlorine

stream is obtained, which is recycled to the phosgene synthesis reactor. The other 5% encompassed in this gas stream mainly is HCl.

Example 1:

HCl is oxidized to chlorine according to the procedure as described in US
5 20100303710 and subsequently purified as described therein.

A chlorine enriched gas mixture (99.9 wt% chlorine, 0.09 wt% O₂) from the just-described oxidation step is fed to a reactor, together with the CO-containing feed stream. The overall feed rates of these streams are 2.53 Nm³/hr and 2.4 Nm³/hr, respectively. The reaction is executed at a pressure of 4.3 bar and a
10 temperature of 64°C, and a mixture consisting of 96.1 wt% phosgene, 3.8 wt% unreacted chlorine and other gases such as carbon dioxide, hydrogen chloride, and hydrogen is obtained.

This mixture is fed to a reactor containing industrial grade propylene glycol (98 wt%, 2 wt% water), which is fed at a rate of 8.9 kg/hr, and a co-feed of pyridine,
15 which is fed at a rate of 46 g/hr. The gas mixture and the liquid components are mixed intimately over a carbon catalyst ex Norit (Cabot Norit Activated Carbon Norit® RB4C). Gaseous HCl is removed from the reactor in a continuous fashion, and is sent to the oxidation step after separation of the higher boiling compounds, which are returned to the reactor.

20 After reaction at 31°C and 1.8 bar, the reaction mixture is fed to a separation section where it is separated via distillation into a carbonate-rich stream, consisting of 99.7 wt% propylene carbonate at a rate of 11.4 kg/hr, a gaseous stream containing HCl and trace amounts of CO₂, and at a rate of 0.4 kg/hr, a minor liquid stream containing mainly unreacted propylene glycol. The latter
25 stream is recycled to the phosgenation reactor without further purification.

Even though the propylene glycol contains 2 wt% of water, with the process according to the present invention, a yield of 99.7 wt% of propylene carbonate based on the theoretical maximum is obtained. Furthermore, due to the configuration of this process negligible amounts of phosgene are emitted.

Finally, due to the closure of the chlorine cycle an environmentally friendly process is obtained.

Claims

1. A process for the preparation of a cyclic organic carbonate comprising:
reacting carbon monoxide and chlorine to form phosgene;
reacting phosgene with a di- or polyhydric alcohol containing a vicinal diol
5 moiety to form a reaction mixture comprising the cyclic organic carbonate
and hydrogen chloride, which reaction proceeds via a chloroformate
intermediate; and
oxidizing the hydrogen chloride to chlorine and water, which chlorine is
recycled to the phosgene synthesis reaction.
- 10 2. The process according to claim 1 wherein the cyclic organic carbonate has
the formula $R^1-O(C=O)O-R^2$, wherein R^1 and R^2 each independently are
aliphatic and/or aromatic hydrocarbon moieties having a backbone of 1 to
12 carbon atoms, which R^1 and R^2 are the same or different and bonded
15 to each other via at least a direct bond forming a 5-membered ring,
containing the carbonate moiety.
3. The process according to claim 1 wherein the di- or polyhydric alcohol
containing a vicinal diol moiety is ethylene glycol, propylene glycol or
glycerol.
4. The process according to any one of the preceding claims further
20 comprising recovering the cyclic organic carbonate from the reaction
mixture.
5. The process according to any one of the preceding claims further
comprising separating the hydrogen chloride from the reaction mixture.
6. The process according to claim 4 or claim 5 wherein the cyclic organic
25 carbonate is recovered after separating the hydrogen chloride from the
reaction mixture.

7. The process according to any one of the preceding claims wherein carbon monoxide and chlorine are reacted at a temperature between 25° and 250°C.
- 5 8. The process according to any one of the preceding claims wherein phosgene and the di- or polyhydric alcohol containing a vicinal diol moiety are reacted at a temperature between -20° and 200°C.
- 10 9. The process according to any one of the preceding claims wherein carbon monoxide and chlorine are reacted in a reactor in the presence of the di- or polyhydric alcohol containing a vicinal diol moiety to form a reaction mixture comprising phosgene, the di- or polyhydric alcohol containing a vicinal diol moiety and the chloroformate intermediate.
- 10 10. The process according to claim 9 wherein the di- or polyhydric alcohol containing a vicinal diol moiety and the chloroformate are further reacted to form the cyclic organic carbonate.
- 15 11. The process according to claim 9 wherein the reaction mixture comprising unreacted di- or polyhydric alcohol containing a vicinal diol moiety and the chloroformate intermediate is fed with additional alcohol to a further reactor, to form the cyclic organic carbonate.
- 20 12. The process according to any one of the claims 1-8 wherein carbon monoxide and chlorine are reacted in a first reactor to form phosgene and the phosgene is reacted with the di- or polyhydric alcohol containing a vicinal diol moiety in a second reactor to form the cyclic organic carbonate.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C07C C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP S61 130288 A (NEOS KK) 18 June 1986 (1986-06-18) cited in the application abstract	1-8,12
A	----- EP 2 067 742 A1 (BAYER MATERIALSCIENCE AG [DE]) 10 June 2009 (2009-06-10) claim 1	1
A	----- EP 1 170 250 A1 (SUMITOMO CHEMICAL CO [JP]) 9 January 2002 (2002-01-09) cited in the application claim 1 paragraph [0002]	1
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Further documents are listed in the continuation of Box C.

See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/062456

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 992 592 A2 (BAYER MATERIALSCIENCE AG [DE]) 19 November 2008 (2008-11-19) claim 1 paragraph [0002] -----	1
A	EP 2 371 807 A1 (BAYER MATERIALSCIENCE AG [DE]) 5 October 2011 (2011-10-05) cited in the application claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/062456

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