

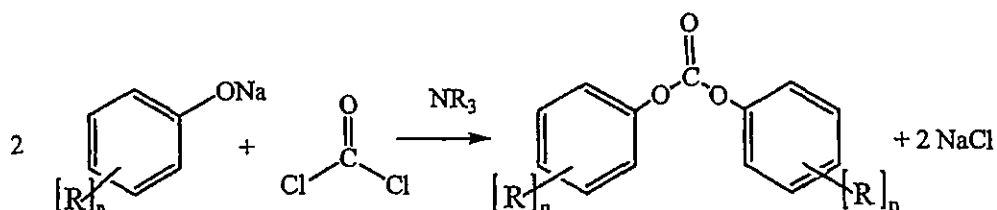
TITLE OF THE INVENTION

Processes for the Production of Diaryl Carbonates and Treatment of
Alkalichloride Solutions Resulting Therefrom

BACKGROUND OF THE INVENTION

5 [0001] The invention relates, in general, to a combined process for the production of diaryl carbonate and electrolysis of alkali chloride-containing process wastewater. The invention also relates, more particularly, to processes for the treatment of alkali chloride-containing waste solutions for further use in a diaryl carbonate production process, and even more particularly, a diphenyl carbonate production process ("DPC process").

10 [0002] The production of diaryl carbonates, and more particularly diphenyl carbonates, generally takes place by a continuous process, by the production or introduction of phosgene and subsequent reaction of monophenols and phosgene in an inert solvent in the presence of alkali and a nitrogen catalyst at the reaction interface, according to the following general reaction scheme:



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[0003] The production of diaryl carbonates, *e.g.*, by interfacial polycondensation, is described in various literature sources, *e.g.*, in "Chemistry and Physics of Polycarbonates", POLYMER REVIEWS, H. Schnell, Vol. 9, John Wiley and Sons, Inc. (1964) pp. 50-51, the entire contents of which are incorporated herein by reference.

20 [0004] Processes for the production of diaryl carbonates operated at temperatures of $>65^\circ\text{C}$ are known. The pH can be adjusted initially to a low value (pH ~ 8 to 9) in such processes and then to a higher value (pH ~ 10 to 11).

[0005] Optimizations of such a process by improved intermixing, maintaining a narrow temperature and pH profile, and/or isolation of the product, are also known.

[0006] In such known processes, however, a high residual phenol value in the wastewater, which can pollute the environment and confront the sewage works with

5 increased wastewater problems, makes costly purification operations necessary. Thus, removal of organic impurities in the wastewater by an extraction with methylene chloride has been suggested in the literature. The alkali chloride-containing waste solution is generally freed of solvents and organic residues and is then disposed of.

[0007] It is also known, however, that the sodium chloride-containing wastewaters
10 can be purified by ozonolysis and are then suitable for use in sodium chloride electrolysis. A disadvantage of ozonolysis is that such processes can be very cost-intensive.

[0008] It is also known that a sodium chloride-containing wastewater stream can be evaporated until all the water has been removed and the remaining salt, together with the organic impurities, can be subjected to a heat treatment as a result of which the organic
15 components are destroyed. The use of infrared radiation for such processes can be preferred. A disadvantage of such processes is that the water has to be completely evaporated, and so the processes cannot be carried out economically.

[0009] It is also known that the wastewater from a DPC production can be purified by extraction and then fed into sodium chloride electrolysis. However, only a maximum of 26%
20 of the sodium chloride is known to be recoverable from the wastewater from DPC production by such processes, since if greater quantities were recovered, the water introduced into the electrolysis with the wastewater would bring the water balance of the sodium chloride electrolysis out of equilibrium.

[0010] Sodium chloride-containing solutions formed during DPC production
25 typically have a sodium chloride content of 13 to 17 wt.%. Thus, the sodium chloride present in the solutions can never be completely recovered by known processes. With a sodium chloride concentration of 17 wt.%, in a standard sodium chloride electrolysis using a commercial ion exchange membrane having a water transport of 3.5 moles of water per mole

of sodium, only approx. 23% of the sodium chloride from the sodium chloride-containing solutions is successfully used. Even by concentrating up to a saturated sodium chloride solution of approx. 25 wt.%, only a recycling quota of 38% of the sodium chloride contained in the sodium chloride-containing solution would be achieved. No complete recycling of the sodium chloride-containing solution has become known. It has also been suggested that the sodium chloride-containing solution can be evaporated by means of thermal processes in such a way that a highly concentrated sodium chloride solution can be fed into an electrolytic cell. However, the evaporation is energy-intensive and costly.

[0011] Thus, there is a need in the art to provide a diaryl carbonate production process which provides products in high purity and good yield and, at the same time, represents a reduction in environmental pollution or wastewater problems at the production area's sewage works by maximized recycling of alkali chloride from alkali chloride-containing process wastewater solutions obtained from diaryl carbonate production.

[0012] Moreover, there is a need, during the recycling, to provide processes which require minimal energy input, thus also conserving resources.

SUMMARY OF THE INVENTION

[0013] It has been found that the alkali chloride-containing wastewater solutions forming during the continuous production of diaryl carbonates, such as by reaction of monophenols and phosgene in an inert solvent in the presence of alkali and amine catalyst at the interface, can be fed directly into an electrochemical oxidation of the alkali chloride obtained to form chlorine, alkali hydroxide solution and optionally hydrogen without costly purification. It has been found that this can be accomplished by introduction of the wastewater solution into an electrochemical oxidation after adjustment of the pH of the solution to a value less than or equal to 8 and simple treatment with an adsorbent, such as activated carbon. The chlorine obtained from the electrochemical oxidation can be recycled into the production of phosgene. Moreover, the alkali hydroxide solution can be recycled into the diaryl carbonate production reaction as basic catalyst.

[0014] One embodiment of the present invention includes a process comprising: (a) reacting phosgene and a monohydroxyl aryl compound in the presence of a suitable catalyst to form a diaryl carbonate and a solution comprising an alkali chloride; (b) separating the diaryl carbonate from the solution; (c) adjusting the pH of the solution to a value of less than or equal to 8 to form a pH-adjusted solution; (d) treating the pH-adjusted solution with an adsorbent to form a treated solution; (e) subjecting at least a portion of the treated solution to electrochemical oxidation to form chlorine and an alkali hydroxide solution; and (f) recycling at least a portion of one or both of the chlorine and the alkali hydroxide solution.

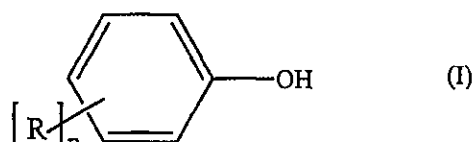
[0015] Another embodiment of the present invention includes a process comprising: (a) reacting phosgene and a monohydroxyl aryl compound in the presence of a suitable catalyst to form a diaryl carbonate and a solution comprising an alkali chloride; (b) separating the diaryl carbonate from the solution; (c) adjusting the pH of the solution with hydrogen chloride to a value of less than or equal to 7 to form a pH-adjusted solution; (d) treating the pH-adjusted solution with an adsorbent to form a treated solution; (e) subjecting at least a portion of the treated solution to electrochemical oxidation to form chlorine and an alkali hydroxide solution; and (f) recycling at least a portion of one or both of the chlorine and the alkali hydroxide solution; wherein recycling at least a portion of the chlorine comprises feeding the portion to a reaction with carbon monoxide to form at least a portion of the phosgene reacted with the monohydroxyl aryl compound; wherein recycling at least a portion of the alkali hydroxide solution comprises feeding the portion to the reaction of the phosgene and the monohydroxyl aryl compound; and wherein the electrochemical oxidation is carried out at a current density of 2 to 6 kA per m² of membrane; a temperature of 70 to 100°C; an absolute pressure of 1.0 to 1.4 bar; and a differential pressure between an anode compartment and a cathode compartment of 20 to 150 mbar.

DETAILED DESCRIPTION OF THE INVENTION

[0016] As used herein, the singular terms “a” and “the” are synonymous and used interchangeably with “one or more.” Accordingly, for example, reference to “a gas” herein

or in the appended claims can refer to a single gas or more than one gas. Additionally, all numerical values, unless otherwise specifically noted, are understood to be modified by the word "about."

- 5 [0017] Preferred monohydroxyl aryl compounds which are suitable for use in various embodiments of the processes according to the invention include phenol compounds of the general formula (I):



wherein each R independently represents a hydrogen, a halogen or a branched or unbranched C₁ to C₉ alkyl group, alkoxy group, carbonyl group or alkoxycarbonyl group, and n represents an integer of 0 to 5.

- 10 [0018] Preferred phenol compounds of the general formula (I) which can be used in processes according to the invention include phenol, alkylphenols such as cresols, p-tert.-butylphenol, p-cumylphenol, p-n-octylphenol, p-isooctylphenol, p-n-nonylphenol and p-isononylphenol, halophenols such as p-chlorophenol, 2,4-dichlorophenol, p-bromophenol and 2,4,6-tribromophenol or methyl salicylate are preferred. Phenol is particularly preferred.
- 15 [0019] Suitable catalysts for the reaction of phosgene and a monohydroxyl aryl compound to form a phenolate include basic compounds, such as for example, alkali hydroxides. Suitable alkali hydroxides include sodium hydroxide, potassium hydroxide and lithium hydroxide. Suitable hydroxides, most preferably sodium hydroxide, can be used as a solution, and are preferably used as a 10 to 55 wt.% solution.
- 20 [0020] The reaction of phosgene and a monohydroxyl aryl compound can be accelerated by additional catalytic components, such as tertiary amines, N-alkylpiperidines and/or onium salts. Tributylamine, triethylamine and N-ethylpiperidine are preferably used.
- [0021] The amine catalyst used can be open-chained or cyclic, triethylamine and ethylpiperidine being particularly preferred. The amine catalyst is preferably used as a 1 to 55
- 25 wt.% solution.

[0022] The term "onium salts" as used herein refers to compounds such as NR_4X , wherein R can be an alkyl and/or aryl group and/or an H, and X is an anion.

[0023] Phosgene to be reacted with a monohydroxyl aryl compound can be introduced to the reaction in liquid or gaseous form or dissolved in an inert solvent.

5 [0024] Inert organic solvents that can preferably be used in the processes of the invention include, for example, dichloromethane, toluene, the various dichloroethanes and chloropropane compounds, chlorobenzene and chlorotoluene. Dichloromethane is preferably used.

10 [0025] The reaction of phosgene and a monohydroxyl aryl compound is preferably carried out continuously and particularly preferably in a plug flow without any significant back mixing. This can therefore take place, e.g., in tubular reactors. The intermixing of the two phases (aqueous and organic phase) can be achieved, for example, by inbuilt pipe baffles, static mixers and/or e.g. pumps.

15 [0026] The reaction of phosgene and a monohydroxyl aryl compound particularly preferably takes place in two stages.

20 [0027] In a first stage of such preferred embodiments, the reaction is started by bringing together the feedstocks of (i) phosgene, (ii) an inert solvent, which preferably acts first as a solvent for the phosgene, and (iii) a monohydroxyl aryl compound, which is preferably already previously dissolved in the alkali hydroxide solution. The residence time in the first stage can typically be 2 seconds to 300 seconds, particularly preferably 4 seconds to 200 seconds. The pH during the first stage is preferably adjusted by the alkali lye/monophenol/phosgene ratio such that the pH is 11 to 12, preferably 11.2 to 11.8, particularly preferably 11.4 to 11.6. The reaction temperature during the first stage, via cooling, is preferably $<40^\circ\text{C}$, particularly preferably $<35^\circ\text{C}$.

25 [0028] In a second stage of such preferred embodiments, the reaction to form a diaryl carbonate is completed. The residence time in the second stage can typically be 1 minute to 2 hours, preferably 2 minutes to 1 hour, especially preferably 3 minutes to 30 minutes. The second stage can be regulated by constant monitoring of the pH value (preferably measured

online in the continuous process by known methods) and corresponding adjustment of the pH value by addition of alkali hydroxide. The quantity of alkali hydroxide introduced can preferably be adjusted such that the pH of the reaction mixture in the second stage is 7.5 to 10.5, preferably 8 to 9.5, especially preferably 8.2 to 9.3. The reaction temperature of the second stage is preferably <50°C, particularly preferably <40°C, especially preferably <35°C, by cooling.

[0029] Broad ranges, preferred ranges, more preferred ranges and most preferred ranges described herein for various process parameters can be combined with one another as desired, in other words, general conditions for one parameter can be employed with preferred values for another parameter, and more preferable values for another parameter.

[0030] In various preferred embodiments of the invention, phosgene can be reacted with a monohydroxyl aryl compound in a molar ratio of phosgene to monohydroxyl aryl compound of 1 : 2 to 1 : 2.2. Solvent can be mixed into the reaction such that the diaryl carbonate is present in a 5 to 60% solution, preferably a 20 to 45% solution, after the reaction.

[0031] The concentration of amine catalyst is preferably 0.0001 mol to 0.1 mol, based on the monophenol used.

[0032] After the reaction of phosgene and a monohydroxyl aryl compound, the organic phase containing the diaryl carbonate is preferably washed, generally with an aqueous liquid and optionally repeatedly, and after each washing operation it is separated as far as possible from the aqueous phase. The washing preferably takes place with deionized water. The diaryl carbonate solution is generally cloudy after the washing and separation of the washing liquid. Aqueous liquids can be used as washing liquid for the separation of the catalyst, *e.g.*, a dilute mineral acid such as HCl or H₃PO₄, and deionized water for the further purification. The concentration of HCl or H₃PO₄ in the washing liquid can be, *e.g.*, 0.5 to 1.0 wt.%. The organic phase is washed, for example and preferably, twice.

[0033] As phase-separating devices for separating the washing liquid from the organic phase, separating vessels, phase separators, centrifuges or coalescers or combinations of these devices that are known in principle can be used.

[0034] At this stage of processes according to various embodiments of the invention, without taking into account the solvent still to be separated off, surprisingly high degrees of purity of the diaryl carbonate of >99.85% can be obtained.

5 [0035] In such preferred embodiments of the process according to the invention the wash liquids separated in the separation according to (b) will, optionally after separating catalyst residues and/or organic solvent residues, be recycled to reaction b) of the process according to the invention.

[0036] In this connection the separation and working-up of the diaryl carbonate formed in the reaction of phosgene and a monohydroxyl aryl compound includes according to
10 separation according to (b) preferably at least the following steps:

- (aa) separation of diaryl carbonate-containing organic phase and aqueous alkali chloride-containing waste water solution
- (bb) washing the diaryl carbonate-containing organic phase obtained in step (aa) at least once, preferably at least twice, particularly preferably twice, and separating the
15 respective wash liquid.

[0037] It may possibly be necessary to separate at least one of the wash liquid(s) obtained according to (bb) from catalyst residues and possibly organic solvent residues by adjusting the pH value to at least 9, preferably at least 10, particularly preferably 10 to 11, by adding at least one basic compound, and then extract the solution with at least one inert
20 organic solvent, or preferably subject the solution to a subsequent stripping with steam. Suitable basic compounds for the adjustment of the pH value are for example alkali or alkaline earth metal hydroxides or carbonates. The basic compounds may be used in solid form or in the form of their aqueous solutions. Alkali metal hydroxides, particularly preferably sodium hydroxide, are preferably used.

25 [0038] Preferably at least part of the wash liquid(s) from (bb) will be used as a partial replacement of the water for the preparation of the sodium hydroxide for reaction of phosgene and a monohydroxyl aryl compound according to (a), in particular for adjusting the concentration of the sodium hydroxide for reaction of phosgene and a monohydroxyl aryl

compound according to (a). Preferably at least part of the wash liquid(s) from (bb) will be used to dilute the alkali metal hydroxide prepared according to electrochemical oxidation (e), before this is recycled to the production of diaryl carbonate according to reaction of phosgene and a monohydroxyl aryl compound according to (a). Such preferred embodiments of the process according to the invention, in which the wash liquids separated in separation according to (b) are recycled to the process according to the invention, has the additional advantage of a lower waste water discharge.

[0039] After the synthesis of the diaryl carbonate, the diaryl carbonate is separated off in the form of its solution in an organic solvent which may be used during the synthesis, *e.g.* methylene chloride.

[0040] To obtain a highly pure diaryl carbonate, the solvent can be evaporated. The evaporation can take place in several evaporator steps. This takes place, *e.g.*, by one or more distillation columns arranged in series, in which the solvent is separated from the diaryl carbonate.

[0041] Such purification of the diaryl carbonate can be carried out continuously, for example, in such a way that the bottom temperature in the distillation is 150°C to 310°C, preferably 160 to 230°C. The pressure applied to perform this distillation is particularly 1 to 1000 mbar, preferably 5 to 100 mbar.

[0042] Diaryl carbonates purified in such a manner can be distinguished by particularly high purities (GC >99.95%) and extremely good transesterification performance, so that a polycarbonate of excellent quality can be produced therefrom.

[0043] The use of diaryl carbonates for the production of aromatic oligo/polycarbonates by the melt transesterification process is known from the literature and is described, *e.g.*, in the Encyclopedia of Polymer Science, Vol. 10 (1969), Chemistry and Physics of Polycarbonates, Polymer Reviews, H. Schnell, Vol. 9, John Wiley and Sons, Inc. (1964) and U.S. Pat. No. 5,340,905, the entire contents of each of which are incorporated herein by reference.

[0044] The remaining aqueous alkali chloride-containing waste water solution, after separation of the diaryl carbonate, can be advantageously freed of highly volatile organic

impurities, such as, *e.g.*, residues of the organic solvent used in the synthesis and optionally catalyst, for example by distillation or steam stripping. A wastewater solution then remains with a high content of dissolved sodium chloride (~10-20 wt.%) and dissolved sodium carbonates (~0.3-1.5 wt.%). The carbonates can form, *e.g.*, by hydrolysis of the phosgene as a secondary reaction of diaryl carbonate production. In addition, the wastewater can be contaminated with organic compounds, *e.g.*, with phenols (*e.g.* unsubstituted phenol, and/or alkylphenols).

[0045] The treatment of the previously purified wastewater solution with adsorbents can then preferably take place with activated carbon.

[0046] According to various preferred embodiments of the processes according to the invention, the adjustment (*e.g.*, lowering) of the pH can be performed with hydrochloric acid or hydrogen chloride. The use of less expensive sulfuric acid, which is conceivable in principle but less desirable in the present process, can lead to the formation of sodium sulfate during the lowering of the pH, which would then become concentrated in the anolyte circulation in the subsequent electrolysis. Since, *e.g.*, ion exchange membranes can generally only be operated up to a certain sodium sulfate concentration in the anolyte, according to manufacturer's instructions, more anolyte would have to be discharged than when using hydrochloric acid or hydrogen chloride, the reaction product of which is the desired sodium chloride.

[0047] The alkali chloride electrochemical oxidation (electrolysis) is described in more detail below. The following description is provided as an example relating to the electrolysis of sodium chloride, although, as already stated above, in principle any alkali chloride can be used in the process (particularly LiCl, NaCl, KCl). The use of sodium is preferred in various embodiments of the processes according to the invention.

[0048] Membrane electrolysis processes, conventionally used *e.g.* for the electrolysis of sodium chloride-containing solutions, such as described in Peter Schmittinger, CHLORINE, Wiley-VCH Verlag, 2000, the entire contents of which are incorporated herein by reference, can be used for electrochemical oxidation in accordance with the various

embodiments of the present invention. In such processes, an electrolytic cell divided into two compartments, namely an anode compartment with an anode and a cathode compartment with a cathode, is used. The anode and cathode compartments are separated by an ion exchange membrane. A sodium chloride-containing solution with a sodium chloride
5 concentration of generally more than 300 g/l is introduced into the anode compartment. At the anode, the chloride ion is oxidized to form chlorine, which is passed out of the cell with the depleted sodium chloride-containing solution (approx. 200 g/l). Under the influence of the electrical field, the sodium ions migrate through the ion exchange membrane into the cathode compartment. During this migration, each mole of sodium entrains between 3.5 and
10 4.5 moles of water, depending on the membrane. This leads to the anolyte becoming depleted of water. In contrast to the anolyte, on the cathode side water is consumed by the electrolysis of water to hydroxide ions and hydrogen. The water entering the catholyte with the sodium ions is sufficient to keep the concentration of the sodium hydroxide solution in the discharge at 31 – 32 wt.%, with an intake concentration of 30% and a current density of 4 kA/m². In the
15 cathode compartment, water is electrochemically reduced resulting in the formation of hydroxide ions and hydrogen.

[0049] Alternatively, a gas diffusion electrode can also be used as the cathode, at which oxygen is converted to hydroxide ions with electrons, no hydrogen being formed. With the sodium ions entering the cathode compartment through the ion exchange
20 membrane, the hydroxide ions form sodium hydroxide. A sodium hydroxide solution with a concentration of 30 wt.% is generally fed into the cathode compartment and a sodium hydroxide solution with a concentration of 31 – 32 wt.% is discharged. The aim is to achieve the highest possible concentration of sodium hydroxide solution, since sodium hydroxide solution is generally stored or transported as a 50 wt.% lye. However, commercial
25 membranes are not at present resistant to a lye with a concentration higher than 32 wt.%, and so the sodium hydroxide solution has to be concentrated by thermal evaporation.

[0050] In the case of sodium chloride electrolysis, additional water can be introduced into the anolyte by this sodium chloride-containing solution but only water is discharged into

the catholyte through the membrane. If more water is introduced by the sodium chloride-containing solution than can be transported to the catholyte, the anolyte is depleted of sodium chloride and the electrolysis cannot be operated continuously. With very low sodium chloride concentrations, the secondary reaction of oxygen formation would start.

5 [0051] In order to feed maximum quantities of sodium chloride-containing solutions to the sodium chloride electrolysis economically, it may be useful for the water transport through the membrane to be increased. This can take place by selecting suitable membranes, such as described in U.S. Pat. No. 4,025,405, the entire contents of which are incorporated herein by reference. The effect of increased water transport is that the otherwise
10 conventional addition of water to maintain the lye concentration can be omitted.

[0052] According to U.S. Pat. No. 3, 773,634, the entire contents of which are incorporated herein by reference, with a high level of water transport through the membrane, the electrolysis can be operated when a lye concentration of 31 to 43 wt.% and a sodium chloride concentration of 120 to 250 g/l is used.

15 [0053] A disadvantage of such processes disclosed in the U.S. patents is the lower current efficiency of the processes.

[0054] According to various preferred embodiments of the processes according to the invention, the separation of the dialkyl carbonate from the solution includes phase separation, subsequent removal of solvent and optionally used catalyst by stripping with steam, and the
20 separation is followed by the adjustment of the solution pH, and subsequent treatment with activated carbon. Following this sequence, the alkali chloride-containing wastewater solution (*i.e.*, the pH-adjusted, adsorbent-treated solution) can be fed directly into the electrolysis.

[0055] The processes according to various embodiments of the present invention in
25 which more than 26% of an alkali chloride can be recovered from a wastewater solution by electrolysis is an improvement over known prior art processes in which no more than 26% of the sodium chloride present in the wastewater from DPC production could be used in NaCl electrolysis.

[0056] In various preferred embodiments of the processes of the present invention, water can be removed from the alkali chloride-containing wastewater solution by a concentration process. A process is therefore preferred, characterised in that the alkali chloride-containing solution is concentrated before the electrolysis by membrane distillation processes or reverse osmosis.

[0057] Reverse osmosis for example or, particularly preferably, membrane distillation or membrane contactors can be used, such as described in MELIN; RAUTENBACH, Membranverfahren; SPRINGER, BERLIN, 2003, the entire contents of which are incorporated herein by reference. By combining operation of the electrolytic cells according to the invention and concentration processes, theoretically up to 100% of the sodium chloride can be recovered from the wastewater.

[0058] Processes according to the invention can also be carried out with an alkali chloride electrolysis in which no hydrogen is produced at the cathode but the cathode is replaced by a gas diffusion electrode at which oxygen is reduced to form hydroxide ions.

[0059] If, for example, at an integrated production site which can directly receive one or more of the electrolysis products, no hydrogen is required for chemical reactions, it is possible to omit the forced production of hydrogen. One advantage is an energy saving during electrolysis, which is attributable to the lower electrolysis voltage when using a gas diffusion electrode.

[0060] A sodium chloride-containing solution coming from DPC production generally has a sodium chloride content of up to 17 wt.%, in so far as it is the wastewater from the reaction. If the wastewater from the reaction is combined with the washing water, the NaCl concentration is, for example, approx. 13 wt.%. If the electrolysis supplies the chlorine and the sodium hydroxide solution exclusively for DPC production, only a small part of the sodium chloride-containing wastewater can be used in the electrolysis. Thus, with the conventional ion exchange membranes and the standard operating parameters of sodium chloride electrolysis, only a maximum of 26% of the sodium chloride from a 17 wt.% sodium chloride-containing DPC wastewater can be used. The standard operating parameters of NaCl electrolysis are a

brine concentration in the discharge of 200 to 240 g/l and an NaOH concentration of 31 – 32 wt.%. Up to now, therefore, complete recycling of the sodium chloride formed has been impossible. Concentration by thermal evaporation of the water is not currently economical, since sodium chloride is available as a very inexpensive product.

5 [0061] With a process according to the invention, significantly more than 26% of the sodium chloride from wastewaters formed with a concentration of 17 wt.% can be recycled, in so far as the sodium chloride electrolysis exclusively provides the chlorine and the sodium hydroxide solution for DPC production. Sodium chloride electrolyses are generally operated at integrated chemical production sites in connection with a variety of chlorine consumers, such
10 that a sodium chloride-containing wastewater solution is not necessarily available for recycling from each of the various chlorine consumers. The proportion of reusable sodium chloride from the wastewater can be increased where the sodium chloride electrolysis is not used exclusively to provide the sodium hydroxide solution and chlorine for diaryl carbonate production.

[0062] Another preferred variant of the processes of the invention is that the wastewater
15 from diaryl carbonate production is concentrated by solid alkali chloride and fed into the alkali chloride electrolysis. As a result, more than 50% of the alkali chloride from the DPC wastewater could be reused.

[0063] However, this assumes that the chlorine and the alkali lye are not used exclusively for diaryl carbonate production.

20 [0064] An alkali chloride-containing wastewater with a pH of less than 7 is particularly preferably used in or fed to the electrolysis. The pH adjustment preferably takes place with hydrochloric acid, but can also take place with gaseous hydrogen chloride.

[0065] According to another preferred process embodiment, the NaCl electrolysis can be operated in such a way that an NaCl solution coming from the electrolysis cell has an NaCl
25 concentration of less than 200 g/l. In parallel to this, the sodium hydroxide concentration discharged from the cell can be less than 30 wt.%.

[0066] The water transport through the membrane depends not only on the operating parameters but also on the type of membrane used. In the processes of the invention, those ion

exchange membranes that permit a water transport through the membrane of more than 4.5 moles of water per mole of alkali, preferably sodium, under the conditions of alkali chloride and alkali hydroxide concentration according to the invention are preferably used.

[0067] The current density is calculated based on the area of the membrane and is preferably 2 to 6 kA/m². Anodes with a greater surface area are particularly preferably used. Anodes with a greater surface area are to be understood as those in which the physical surface area is distinctly larger than the projected surface area. Anodes with a greater surface area are, *e.g.*, electrodes with a foam- or felt-like construction. As a result, a very large anodic electrode surface area is offered and the local current density is markedly reduced. The surface area of the anode should preferably be selected such that the local current density based on the physical surface area of the electrode is less than 3 kA/m². The larger the surface area and the lower the local current density, the lower the sodium chloride concentration that can be selected in the brine and the higher the proportion of sodium chloride from the wastewater that can be recycled.

[0068] The pH of the alkali chloride-containing wastewater should preferably be less than 7, particularly preferably from 0.5 to 6, before the electrolysis.

[0069] The alkali chloride electrolysis should be operated in such a way that the alkali chloride concentration of the alkali chloride solution coming from the cell is between 100 and 280 g/l sodium chloride and/or that the concentration of the alkali hydroxide coming from the cell is 13 to 33 wt.%.

[0070] Concentrations enabling the cell to be operated at lower voltages are particularly preferred. For this purpose, the concentration of the alkali chloride solution coming from the cell should preferably be between 110 and 220 g/l alkali chloride and/or the concentration of the alkali hydroxide coming from the cell should be 20 to 30 wt.%.

[0071] The ion exchange membranes used in the electrolysis should preferably have a water transport per mole of sodium of more than 4.0 moles H₂O/mole alkali, particularly preferably 5.5 to 6.5 moles H₂O/mole alkali.

[0072] The process can preferably be operated in such a way that the electrolysis is operated at a temperature of 70 to 100°C, preferably at 80 to 95°C.

[0073] The electrolysis can be operated at an absolute pressure of 1 to 1.4 bar, preferably at a pressure of 1.1 to 1.2 bar.

[0074] The pressure ratios between anode and cathode compartments are preferably selected such that the pressure in the cathode compartment is higher than the pressure in the anode compartment. The differential pressure between cathode and anode compartments should preferably be 20 to 150 mbar, more preferably 30 to 100 mbar.

[0075] With lower alkali chloride concentrations, special anode coatings can also be used. In particular, the coating of the anode can contain, in addition to ruthenium oxide, other precious metal components from subgroups 7 and 8 of the periodic table of elements. For example, the anode coating can be doped with palladium compounds. Coatings based on diamond can also be used.

[0076] The following examples illustrate an embodiment of a process according to the invention based on the sodium chloride-containing wastewater formed during the production of diphenyl carbonate, and are only a reference point rather than a limitation.

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EXAMPLES

[0077] Example 1: Addition of sodium chloride-containing reaction wastewater to sodium chloride electrolysis – addition of a 17 wt.% sodium chloride solution from DPC production

[0078] A mixture of 145.2 kg/h of 14.5 wt.-% sodium hydroxide solution and 48.3 kg/h of phenol are brought together with a solution of 86.2 kg/h of methylene chloride and 27.5 kg/h of phosgene (8 mole % excess based on phenol) in a vertically standing, cooled tubular reactor. This reaction mixture is cooled to a temperature of 33°C and, after an average residence time of 15 seconds, a pH of 11.5 is measured. In the second step of the process, 5.4 kg/h of 50% NaOH are then metered into this reaction mixture so that the pH of the second reaction step is 8.5 after a further residence time of 5 minutes. In the continuously operated reaction, metering fluctuations that occur are offset by adjusting the additions of NaOH in each case. In the second step of the process, the reaction mixture is continuously mixed by passing through a pipe

provided with constrictions. After renewed addition of NaOH, the reaction temperature is adjusted by cooling to 30°C. After separating off the organic from the aqueous phase (reaction wastewater), the DPC solution is washed with 0.6% hydrochloric acid and water. After removing the solvent, 99.9% diphenyl carbonate is obtained. The reaction wastewater is not
5 combined with the washing phases here and is freed of solvent residues and catalyst by stripping with steam. After neutralising with hydrochloric acid and treating with activated carbon, the reaction wastewater contains 17% NaCl and < 2 ppm phenol.

[0079] It can be fed into the sodium chloride electrolytic cell without any further purification.

10 [0080] The electrolysis is performed for example in a laboratory electrolytic cell with an anode area of 0.01 m². The current density was 4 kA/m², discharge temperature on the cathode side 88°C and discharge temperature on the anode side 89°C. An electrolytic cell with a standard anode and cathode coating from DENORA, Germany, was used. A Nafion 982 WX ion exchange membrane from DuPont was used. The electrolytic voltage was 3.02 V. A sodium
15 chloride-containing solution was pumped through the anode compartment at a mass flow rate of 0.98 kg/h. The concentration of the solution fed into the anode compartment was 25 wt.% NaCl. A 20 wt.% NaCl solution could be removed from the anode compartment. 0.121 kg/h of 17 wt.% reaction wastewater from diphenyl carbonate production and 0.0653 kg/h of solid sodium chloride were added to the NaCl solution removed from the anode compartment. The solution
20 was then fed back into the anode compartment. The water transport through the membrane was 3.5 moles of water per mole of sodium.

[0081] On the cathode side, a sodium hydroxide solution was pumped round at a mass flow rate of 1.107 kg/h. The concentration of the sodium hydroxide solution fed into the cathode side was 30 wt.% NaOH and the sodium hydroxide solution removed from the cathode side had
25 a concentration of 32% NaOH. 0.188 kg/h of the 31.9% lye were removed from the volume flow and the remainder was topped up with 0.0664 kg/h of water and fed back into the cathode element.

[0082] 23.3% of the reacted sodium chloride originates from the DPC reaction wastewater.

[0083] Example 2: Addition of sodium chloride-containing reaction wastewater to sodium chloride electrolysis with a gas diffusion electrode – addition of a 17 wt.% sodium chloride solution (reaction wastewater) from DPC production

[0084] The wastewater corresponded to the quality of that according to Example 1. Since no hydrogen is required for the production of DPC, the formation of hydrogen during the electrolysis can be omitted. The electrolysis was therefore operated with gas diffusion electrodes. The current density was 4 kA/m^2 , cathode side outlet temperature 88°C and anode side outlet temperature 89°C . An electrolytic cell with a standard anode coating from DENORA, Germany, was used. A Nafion 982 WX ion exchange membrane from DuPont was used. The electrolytic voltage was 2.11 V. The sodium chloride concentration of the solution removed from the anode compartment was 17 wt.% NaCl. 0.166 kg/h of 17 wt.% reaction wastewater and 0.0553 kg/h of solid sodium chloride were added to the NaCl solution removed from the anode compartment. The solution was then fed back into the anode compartment. The water transport through the membrane was 4.9 moles of water per mole of sodium.

[0085] On the cathode side, a sodium hydroxide solution was pumped round at a mass flow rate of 0.848 kg/h. The concentration of the sodium hydroxide solution fed into the cathode side was 30 wt.% NaOH and the sodium hydroxide solution removed from the cathode side had a concentration of 32 wt.% NaOH. 0.192 kg/h of the 31.2% lye were removed from the volume flow and the remainder was topped up with 0.033 kg/h of water and fed back into the cathode element.

[0086] The proportion of reacted sodium chloride from the DPC reaction wastewater was 32.4%.

[0087] Example 3: Addition of sodium chloride-containing reaction wastewater to sodium chloride electrolysis with a gas diffusion electrode – addition of a 17 wt.% sodium chloride solution (reaction wastewater) from DPC production

[0088] The wastewater corresponded to the quality of that according to Example 1. Since no hydrogen is required for the production of DPC, the formation of hydrogen during the electrolysis can be omitted. The electrolysis was therefore operated with gas diffusion electrodes. The current density was 4 kA/m^2 , cathode side outlet temperature 88°C and anode side outlet temperature 89°C . An electrolytic cell with a standard anode coating from DENORA, Germany, was used. A Nafion 2030 ion exchange membrane from DuPont was used. The electrolytic voltage was 1.96 V. The sodium chloride concentration of the solution removed from the anode compartment was 15 wt.% NaCl. 0.178 kg/h of 17 wt.% reaction wastewater and 0.0553 kg/h of solid sodium chloride were added to the NaCl solution removed from the anode compartment. The solution was then fed back into the anode compartment. The water transport through the membrane was 5.26 moles of water per mole of sodium.

[0089] On the cathode side, a sodium hydroxide solution was pumped round at a mass flow rate of 0.295 kg/h. The concentration of the sodium hydroxide solution fed into the cathode side was 30 wt.% NaOH and the sodium hydroxide solution removed from the cathode side had a concentration of 32 wt.% NaOH. 0.188 kg/h of the 32% lye were removed from the volume flow and the remainder was topped up with 0.0184 kg/h of water and fed back into the cathode element.

[0090] The proportion of reacted sodium chloride from the DPC reaction wastewater was 34.4%.

20 [0091] Example 4: Recycling of wash phases from the DPC working-up in the DPC production – addition of a waste water phase from the acid wash to the DPC production.

[0092] The procedure was carried out as in Example 1, with the difference that, after separating the organic phase from the aqueous phase (reaction waste water), the DPC solution was washed with 0.6 wt.-% hydrochloric acid (acid wash), and then once more with water (neutral wash). The acidic wash phase from the DPC working-up was adjusted to pH 10 with NaOH and was then freed from solvent residues and catalysts by extraction with methylene chloride or by stripping with steam. After the phase separation an aqueous phase

was obtained containing 1.5 wt.-% NaCl, which can be re-used as a partial replacement of the water for the preparation of the 14.5 wt.-% NaOH solution for the DPC production.

[0093] Example 5 : Recycling of wash phases from the DPC working-up to the DPC production – addition of a neutral wash phase to the DPC production.

5 [0094] The procedure was carried out as in Example 4. The neutral wash phase from the DPC working-up can be re-used without further treatment as a partial replacement of the water for the preparation of the 14.5 wt.-% NaOH solution for the DPC production.

[0095] Example 6: Recycling of wash phases from the DPC working-up to the DPC production – addition of the purified waste water phases from the acid and neutral wash to
10 the DPC production.

[0096] The procedure was carried out as in Example 4. The acid and neutral wash phase from the DPC working-up were combined, adjusted to pH 10 with NaOH, and then freed from solvent residues and catalysts by extraction with methylene chloride or by stripping with steam. After phase separation an aqueous phase was obtained containing
15 about 1 wt.-% NaCl, which can be re-used as a partial replacement of the water for the preparation of the 14.5 wt.-% NaOH solution for the DPC production.

[0097] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular
20 embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

What is claimed is:

1. A process comprising:
 - (a) reacting phosgene and a monohydroxyl aryl compound in the presence of a suitable catalyst to form a diaryl carbonate and a solution comprising an alkali chloride;
 - (b) separating the diaryl carbonate from the solution;
 - (c) adjusting the pH of the solution to a value of less than or equal to 8 to form a pH-adjusted solution;
 - (d) treating the pH-adjusted solution with an adsorbent to form a treated solution;
 - (e) subjecting at least a portion of the treated solution to electrochemical oxidation to form chlorine and an alkali hydroxide solution; and
 - (f) recycling at least a portion of one or both of the chlorine and the alkali hydroxide solution.
2. The process according to claim 1, wherein recycling at least a portion of the chlorine comprises feeding the portion to a reaction with carbon monoxide to form at least a portion of the phosgene reacted with the monohydroxyl aryl compound.
3. The process according to claim 1, wherein recycling at least a portion of the alkali hydroxide solution comprises feeding the portion to the reaction of the phosgene and the monohydroxyl aryl compound.
4. The process according to claim 1, further comprising subjecting one or more of the solution, the pH-adjusted solution and the treated solution to a separation to remove an amount of residual solvent.

5. The process according to claim 4, wherein the separation comprises steam stripping.
6. The process according to claim 1, wherein the electrochemical oxidation is carried out with a cathode comprising a gas diffusion electrode.
7. The process according to claim 1, further comprising feeding a portion of the treated solution to a brine circuit of a membrane electrolysis process.
8. The process according to claim 1, further comprising adding additional alkali chloride to the electrochemical oxidation.
9. The process according to claim 1, wherein the pH of the solution is adjusted to a value of less than or equal to 7.
10. The process according to claim 1, wherein adjusting the pH of the solution comprises adding hydrogen chloride.
11. The process according to claim 1, wherein the treated solution prior to electrochemical oxidation has an alkali chloride concentration of 100 to 280 g/L.
12. The process according to claim 1, wherein the alkali hydroxide solution has an alkali hydroxide concentration of 13 to 33 wt.%.
13. The process according to claim 11, wherein the alkali hydroxide solution has an alkali hydroxide concentration of 13 to 33 wt.%.

14. The process according to claim 1, wherein the electrochemical oxidation is carried out using an ion exchange membrane having a water transport value greater than 4 moles H₂O per mole of alkali ion.

15. The process according to claim 1, wherein the electrochemical oxidation is carried out using an ion exchange membrane having a water transport value of 5.5 to 6.5 moles H₂O per mole of alkali ion.

16. The process according to claim 1, wherein the electrochemical oxidation is carried out at a current density of 2 to 6 kA per m² of membrane.

17. The process according to claim 15, wherein the electrochemical oxidation is carried out at a current density of 2 to 6 kA per m² of membrane.

18. The process according to claim 1, wherein the electrochemical oxidation is carried out at a temperature of 70 to 100°C.

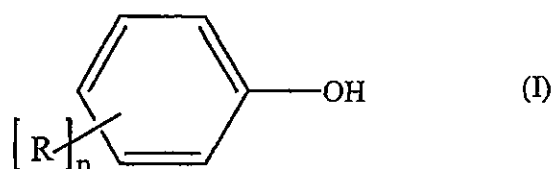
19. The process according to claim 1, wherein the electrochemical oxidation is carried out at a differential pressure between an anode compartment and a cathode compartment of 20 to 150 mbar.

20. The process according to claim 1, wherein the electrochemical oxidation is carried out using an anode having a coating comprising ruthenium oxide and a compound of an element selected from the group consisting of Group 4 elements, Group 7 elements, Group 8 elements, and combinations thereof.

21. The process according to claim 1, wherein the electrochemical oxidation is carried out using an electrolysis cell having an anode and a membrane, and wherein the anode has a surface area greater than a surface area of the membrane.

22. The process according to claim 1, wherein the electrochemical oxidation is carried out at a current density of 2 to 6 kA per m² of membrane; a temperature of 70 to 100°C; an absolute pressure of 1.0 to 1.4 bar; and a differential pressure between an anode compartment and a cathode compartment of 20 to 150 mbar.

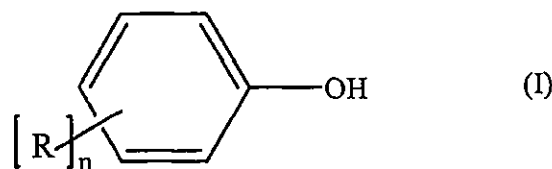
23. The process according to claim 1, wherein the monohydroxyl aryl compound comprises a phenol compound of the general formula (I):



wherein each R independently represents a substituent selected from the group consisting of hydrogen, halogens, C₁₋₉ alkyl groups, C₁₋₉ alkoxy groups, C₁₋₉ carbonyl groups, and C₁₋₉ alkoxycarbonyl groups; and n represents an integer of 0 to 5.

24. A process comprising:

(a) reacting phosgene and a phenol compound of the general formula (I) in the presence of a suitable catalyst to form a diaryl carbonate and a solution comprising an alkali chloride;



wherein each R independently represents a substituent selected from the group consisting of hydrogen, halogens, C₁₋₉ alkyl groups, C₁₋₉ alkoxy groups, C₁₋₉ carbonyl groups, and C₁₋₉ alkoxycarbonyl groups; and n represents an integer of 0 to 5;

- (b) separating the diaryl carbonate from the solution;
- (c) adjusting the pH of the solution with hydrogen chloride to a value of less than or equal to 7 to form a pH-adjusted solution;
- (d) treating the pH-adjusted solution with an adsorbent to form a treated solution;
- (e) subjecting at least a portion of the treated solution to electrochemical oxidation to form chlorine and an alkali hydroxide solution; and
- (f) recycling at least a portion of one or both of the chlorine and the alkali hydroxide solution;

wherein recycling at least a portion of the chlorine comprises feeding the portion to a reaction with carbon monoxide to form at least a portion of the phosgene reacted with the monohydroxyl aryl compound; wherein recycling at least a portion of the alkali hydroxide solution comprises feeding the portion to the reaction of the phosgene and the monohydroxyl aryl compound; and wherein the electrochemical oxidation is carried out at a current density of 2 to 6 kA per m² of membrane; a temperature of 70 to 100°C; an absolute pressure of 1.0 to 1.4 bar; and a differential pressure between an anode compartment and a cathode compartment of 20 to 150 mbar.

25. The process according to claim 1, wherein the separation of the diaryl carbonate from the solution according to (b) comprises at least the following steps:

- (aa) separation of diaryl carbonate-containing organic phase and aqueous alkali chloride-containing waste water solution
- (bb) washing the diaryl carbonate-containing organic phase obtained in step (aa) at least once,

and wherein at least part of the wash phase(s) from (bb) is used, optionally after separating catalyst residues and possibly organic solvent residues, as a partial replacement of the water for the production of the sodium hydroxide for the reaction of phosgene and a monohydroxyl aryl compound according to (a).