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(54) Title: PROCESS FOR PREVENTING MEMBRANE DEGENERATION USING COMPLEXING AGENTS

(57) Abstract: Membrane cell electrolysis process to prepare chlorine from an aqueous salt solution comprising the steps of dissolving a sodium chloride source in water to form an aqueous salt solution comprising sodium chloride, and dosing one or more degeneration reducing agents selected from the group consisting of monosaccharides, oligosaccharides, polysaccharides, polycarboxylic acids, polyacrylates, polymaleic acids, and derivatives thereof to said aqueous salt solution in a total amount of, on average, between 0.1 mg and 1,000 mg per litre of aqueous salt solution at a stage of the electrolysis process where the amount of active chlorine dissolved in said aqueous salt solution is less than 1.5 g per litre of aqueous salt solution and/or to the membrane cells, in order to reduce fouling and/or clogging of the membrane in said membrane cell.



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## PROCESS FOR PREVENTING MEMBRANE DEGENERATION USING COMPLEXING AGENTS

5 The invention relates to a process for preventing the degeneration of membranes in electrolysis plants for the production of chlorine during operation using certain complexing agents.

Chlorine is an important industrial chemical used to produce pesticides,  
10 disinfectants, chlorine bleach cleaners, swimming pool chemicals, PVC plastic, synthetic rubber, and other chlorinated chemicals. Chlorine can be prepared from an aqueous sodium chloride solution (brine) by electrolysis, giving caustic soda and hydrogen as byproducts. Three methods for the extraction of chlorine by electrolysis are used industrially. Mercury cell electrolysis was the first  
15 method used to produce chlorine on an industrial scale. Titanium anodes are located above a liquid mercury cathode and a solution of sodium chloride is positioned between the electrodes. When an electrical current is applied, chloride is released at the titanium anodes, while the sodium dissolves into the mercury cathode forming an amalgam. However, this method consumes vast  
20 amounts of energy and there are also concerns about mercury emissions. A second method is diaphragm cell electrolysis, where an asbestos diaphragm is deposited on an iron grid cathode to prevent the chlorine forming at the anode and the sodium hydroxide forming at the cathode from re-mixing. This method uses less energy than the mercury cell, but the sodium hydroxide is not as  
25 easily concentrated and precipitated into a useful substance. A third method is membrane cell electrolysis, which eliminates the need for mercury and asbestos as process materials and enables greater energy efficiency. In said method, the electrolysis is performed in electrolysis cells which are divided into two by a membrane acting as an ion exchanger. Saturated sodium chloride solution is  
30 placed in the anode compartment, while a caustic solution is placed in the cathode compartment. Nowadays, this third method is the most preferred one.

However, the electrolyser membranes and electrodes are extremely sensitive to impurities in the brine, particularly multivalent metal ions. Both cell voltage and current efficiency are sensitive to alkaline earth metals such as calcium and magnesium. Generally, multivalent metal cations are soluble at the relatively low pH levels on the feed side of the membrane and are thus able to enter the membrane. The cations flow with water and sodium ions from the anode compartment into the membrane towards the cathode. However, because of their limited solubility at the higher pH levels that prevail inside the membrane, the multivalent metal cations will precipitate inside the membrane, causing irreversible damage to the membrane.

Not only inorganic contaminants form a problem. Also traces of organic compounds, for example originating from the agent employed to prevent the sodium chloride from caking, traces of retarding agents or crystal growth inhibitors occluded in the salt, residual solvents, etc., can cause problems. When a brine solution containing one or more of such contaminants is electrolysed, the organic species may precipitate on the surface of and within an electrolysis cell membrane to cause plugging. Organic compounds may also interfere with the electrodes, increasing the energy consumption or reducing the lifetime of electrodes. The formation of undesired chlorinated compounds from organic compounds in the brine might also be a problem. Hence, to achieve a maximum life-time for a membrane in an electrolysis cell, the concentration of contaminating organic compounds and multivalent metal cations in the feed-brine solution must be reduced to as low a level as economically possible.

In general, a brine treatment is therefore to be performed to reduce the content of organic contaminations and also a treatment to reduce brine "hardness", *i.e.* to reduce the levels of calcium, magnesium, and strontium ions present in the brine to below about 20 ppb for calcium and magnesium ions, commonly employed upper specification limits for these alkaline earth metal ions in brine serving as feedstock in a chlor-alkali plant. Furthermore, sodium chlorate is produced to a small extent during electrolysis and must also be controlled. Therefore, brine preparation and treatment typically consist of the following

steps. In a first step raw salt (sodium chloride) is dissolved in a mixture of water and depleted, dechlorinated brine, *i.e.* brine which after having left the electrolysis cells is dechlorinated and subsequently recycled, to produce a saturated brine solution. Depending on the concentration of contaminants, the  
5 brine solution, optionally after dilution with water, is first subjected to a treatment wherein alkaline earth and transition metals are precipitated as their carbonates and/or hydroxides, followed by a filtering or settling process such as clarification. A further treatment is necessary wherein essentially all the remaining calcium, strontium, and magnesium impurities are removed. This  
10 treatment is typically performed using chelating ion exchange resins having a high affinity for alkaline earth metal ions.

It was found that transition metal impurities present in the brine, originating for example from iron-containing non-caking agents or present in the water stream  
15 used to prepare the brine, are only partially bound by the Ca, Sr, and/or Mg-removing ion exchanger. Thus, in spite of the above-mentioned purification treatments, the brine which is to be fed to the electrolysis cells will still comprise a significant residual amount of these transition metal ions, such as Fe(II), Fe(III), and/or Al(III) ions. These transition metal contaminations present  
20 in the brine normally have a strong tendency to precipitate, *int. al.* as oxides and/or hydroxide complexes. As mentioned above, because of the differences in pH values at the cathode side and the anode side of the membrane, the transition metal ions will normally precipitate on the surface of the membrane at the anode side and inside the membrane, causing degeneration of the  
25 membrane. As a consequence, the energy consumption will gradually increase, while the production of chlorine will gradually decrease due to a decreased current efficiency, until the membrane is fouled to such an extent that it needs cleaning or replacing. Hence, if one were able to slow down the fouling rate of the membranes, or even more preferably, if one were able to prevent the  
30 membranes from becoming fouled at all, the overall production capacity would increase while the overall energy consumption would decrease. Moreover, one

would save on the costs of early replacement of the membranes, both in terms of production time and membrane costs.

5 It is therefore an object of the present invention to provide a membrane electrolysis process for the preparation of chlorine from an aqueous salt solution comprising sodium chloride wherein fouling and/or clogging of the membrane during processing is reduced and, preferably, wherein degeneration of the membrane due to the presence of transition metal ions in the electrolysis cells is completely prevented.

10

It has now surprisingly been found that the extent of fouling and clogging, and thus of the degeneration of a membrane in a membrane electrolysis cell during the preparation of chlorine from an aqueous salt solution comprising sodium chloride can be reduced or, preferably, even completely prevented, if certain  
15 additives are dosed to said aqueous salt solution which are able to complex alkali earth metal ions and/or transition metal ions (*i.e.* they serve as complexing agents for these metal ions). It was found that the selected complexing agents according to the present invention decompose in the presence of chlorine into components that cause no worry in the chlor-alkali  
20 process and, as a consequence, that these complexing agents do not foul the membranes themselves. The complexing agents according to the present invention can even be dosed to the aqueous salt solution if dissolved active chlorine is present therein. It was surprisingly found that if, on average, a total amount of between 0.1 and 1,000 mg of the selected complexing agent(s)  
25 according to the present invention is dosed per litre of said aqueous salt solution complexing agents according to the present invention to the aqueous salt solution at a stage in the electrolysis process at which said aqueous salt solution does not contain more than 1.5 g of active chlorine dissolved per litre of that aqueous salt solution and/or is dosed directly to the membrane cells, a  
30 sufficient amount of complexing agent will be present inside the membrane cells in order to reduce, preferably prevent, fouling and/or clogging of the membrane by alkali earth metal ions and/or transition metal ions present in the brine.

Accordingly, it was found that the membrane needs to be cleaned less frequently, and less aggressive cleaning products can be used. Furthermore, the membrane lifetime and the current efficiency were found to increase, while the cell voltage was decreased. Moreover, the process according to the present invention has the advantage that it can be implemented in conventional electrolysis plants without necessitating extended adaptations of the installations.

Accordingly, the present invention relates to a membrane cell electrolysis process to prepare chlorine from an aqueous salt solution comprising the steps of dissolving a sodium chloride source in water to form an aqueous salt solution comprising sodium chloride, and dosing one or more special complexing agents selected from the group consisting of monosaccharides, oligosaccharides, polysaccharides, polycarboxylic acids, polyacrylates, polymaleic acids, and derivatives thereof to said aqueous salt solution in a total amount of, on average, between 0.1 mg and 1,000 mg per litre of aqueous salt solution at a stage of the electrolysis process where the amount of active chlorine dissolved in said aqueous salt solution is less than 1.5 g per litre of aqueous salt solution and/or to the membrane cells, in order to reduce fouling and/or clogging of the membrane in said membrane cell. It is noted that the aqueous salt solution comprising sodium chloride is hereinafter also denominated as "brine feed" or simply "brine".

A complexing agent selected from the group consisting of monosaccharides, oligosaccharides, polysaccharides, polycarboxylic acids, polyacrylates, polymaleic acids, and derivatives thereof and which does not comprise any carboxylic acid groups should pass test 1 or test 2, and preferably, it should pass both test 1 and test 2, in order to be suitable for use according to the present invention:

30

- 1) To 1 litre of saturated brine having a pH of 2, 150 ppb  $\text{FeCl}_3$  based on the amount of Fe(III) are added. Furthermore, 100 ppm of complexing agent

are added. Subsequently, a sodium hydroxide solution is added until the pH is 5.5. The mixture is filtered through a 0.45 micron pore size Millex-HA syringe driven filter unit and the filtered brine is analysed for Fe concentration by conventional ICP (Inductively Coupled Plasma) spectrometry. If less than 50 ppb of Fe(III) is found in the solution, then the complexing agent is considered to have passed test 1. It is noted that if the complexing agent is to be used in an electrolysis process which is performed under alkaline conditions, said test should be performed as follows: To 1 litre of saturated brine having a pH of 2, 150 ppb FeCl<sub>3</sub> based on the amount of Fe(III) are added. Furthermore, 100 ppm of complexing agent are added. Subsequently, a sodium hydroxide solution is added until the pH is 10. The mixture is filtered through a 0.45 micron pore size Millex-HA syringe driven filter unit and the filtered brine is analysed for Fe concentration by conventional ICP (Inductively Coupled Plasma) spectrometry. If less than 50 ppb of Fe(III) is present in the solution, the complexing agent is considered to have passed test 1 as well.

2) 1 litre of synthetic electrolysis brine is produced by dissolution of 310 g of sodium chloride, 420 µg of Al(III) ex AlCl<sub>3</sub>, 1,600 µg of Ca(II) ex CaCl<sub>2</sub>, 260 µg of Mg(II) ex MgCl<sub>2</sub>, and 370 µg of Sr(II) ex SrCl<sub>2</sub> in distilled water. All chemicals are ultrapure products ex Merck. The pH of the solution is adjusted to pH=10 by the use of a 1 M sodium hydroxide solution. Subsequently, 2 ml of a dispersion of ion exchanger Lewatit TP 208 in water comprising between 40 - 50% by weight of ion exchanger are added to the solution, together with 200 ppm of complexing agent. The solution is gently shaken using standard laboratory shaking equipment for a time period of about 20 h. Finally, samples are taken using an injection syringe. The solution in the syringe is filtered through a 0.45 micron pore size Millex-HA syringe driven filter unit and the filtered brine is analysed for Ca, Mg, and Sr ion concentrations by conventional ICP (Inductively Coupled Plasma) spectrometry.

If the concentrations of Ca, Mg, and Sr ions are reduced by at least 80% compared to the concentration of these ions originally present in the synthetic electrolysis brine, the complexing agent is considered to have passed test 2.

5

If a complexing agent comprises one or more carboxylic acid groups, an additional requirement is that it should also pass test 3 in order to be suitable for use according to the present invention:

- 10 3) A feed brine containing 300 g/l of NaCl, 300 ppm of a carboxylic acid group-containing complexing agent, 0.72 ppm of Mg, 5.8 ppm of Ca, 1.90 ppm of Fe is prepared. The pH of the brine is 10.3. An ion exchange step is performed on this brine at 60°C to treat the brine for hardness. An aminomethyl phosphonic acid-functionalised chelating ion exchange resin
- 15 (AMP type resin; 50 g resin) is used for this purpose. The ion exchange step is performed at a feed rate of 14 g/min (12.6 bed volumes / h).  
If after 24 hours the concentration of Fe is less than 100 ppb, the complexing agent is considered to have passed test 3.

- 20 A complexing agent which fulfills the above-mentioned requirements is hereinafter denoted as a degeneration reducing agent.

If a complexing agent which does not fulfill the above-mentioned requirements were to be used in a conventional chlor-alkali electrolysis process, various

25 problems can arise such as the accumulation of organic material in the cells, which is undesired, or disruption of the brine purification treatment. This is illustrated for example by US 6,103,092 and US 2001/0011645, where a method to maximize membrane lifetime and efficiency of electrolysis cell operation is disclosed wherein the metal ion concentration in the brine solution

30 used as feedstock for the electrolysis is reduced by subjecting a brine solution containing a metal chelating agent, *i.e.* a complexing agent, such as N,N,N',N'-ethylenediamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA) or sodium



gluconate, to a series of purification steps. It is disclosed that by addition of a chelating agent such as gluconate anion to brine comprising alkali earth metal and transition metal ion-containing contaminants, water-soluble complexes are formed with a fraction of the multivalent transition metal cations such as Fe(III), Ni(II), and Cr(III). Complexation thus is beneficial in that it hinders transition metal salts from precipitating in the manufacturing equipment. With iron(III) for example, gluconate anion forms a strong iron-gluconate complex, thereby solubilising iron in the brine solution. However, when such a brine solution is purified for use in an electrolysis cell by subjecting it to a primary brine treatment in order to remove alkaline earth metals such as calcium and magnesium present in the brine either by passing it through an ion exchange resin or by elevating the pH to precipitate the calcium and magnesium as their carbonates and/or hydroxides, problems will arise. In more detail, the fraction of a transition metal species such as iron(III) present as a gluconate complex remains strongly chelated and will therefore not be removed in said purification step. When brine containing transition metal-gluconate complexes enters an electrolysis cell containing a membrane, the gluconate is substantially destroyed, and at least a portion of each transition metal, such as iron, still precipitates on the surface of and inside the membrane, thus degenerating the membrane. Furthermore, it was observed that when feed brine contains both iron and gluconate, the ion exchange resin used in the primary brine treatment step is also unable to remove hardness as effectively as it would do without the presence of the chelating agent. In the methods according to US 6,103,092 and US 2001/0011645, besides a primary brine treatment step, an additional brine purification step should therefore be performed wherein the brine is passed through a functionalised resin to remove a fraction of the multivalent metal ion contaminants present in the brine in the form of water-soluble complexes with metal chelating agent. Hence, conventional electrolysis plants, where typically only a primary brine purification section is present, require transformation before the just-mentioned processes can be performed, which is undesirable.

On the other hand, the presence of nitrogen in chelating agents such as EDTA or NTA will lead to the formation of  $\text{NCl}_3$  in the electrolysis cells, leading to the formation of explosive gas mixtures, which is also undesirable.

- 5 According to a non-binding theory, the degeneration reducing agents according to the present invention function as follows inside the membrane electrolysis cells of a chlor-alkali plant. The degeneration reducing agents will be decomposed due to the presence of chlorine at the anode side of the membrane. During decomposition, besides  $\text{CO}_2$ ,  $\text{HCl}$ , and water, compounds
- 10 comprising carboxylic end groups will be formed. Said acid groups will complex the transition metal ions present in the brine. As a result, the transition metal(s), preferably  $\text{Fe(III)}$ , will be prevented from forming oxide or hydroxide complexes which might clog the membrane.
- 15 The degeneration reducing agents of the present invention have the advantage that they can be dosed to the feed brine before the brine is subjected to brine purification steps such as purification using an ion exchanger. This is because they merely form a relatively weak complex with transition metal ions. Hence, when the brine comprising the contaminants as well as the degeneration
- 20 reducing agent(s) is fed to an ion exchanger for reduction of "hardness", the degeneration reducing agent will release all alkali metal ions and/or transition metal ions. Subsequently, these ions will be removed by this treatment. For example, when in the primary brine purification the brine is passed through an ion exchanger, these ions will be absorbed by said ion exchanger to the largest
- 25 possible extent. The degeneration reducing agent(s), however, will remain dissolved in the brine. Hence, the residual amount of transition metal ions in the brine not bound by the ion exchanger will be confronted with an excess of degeneration reducing agent, which will complex these ions. As a result, almost
- 30 no free transition metal ions will remain in the resulting brine which is fed to the membrane electrolysis cells, and, consequently, there will be a reduced level of precipitation of transition metal oxides and/or hydroxides in the membrane process.

As mentioned above, suitable degeneration reducing agents can be found among saccharides, polycarboxylic acids, and derivatives thereof. Preferably, saccharides are used. It is noted that the term "saccharide" as used throughout  
5 the specification is meant to include monosaccharides (i.e. carbohydrates which usually possess 3 - 9 carbon atoms), oligosaccharides (i.e. carbohydrates which usually possess 2 - 20 monosaccharide units), and polysaccharides (i.e. carbohydrates possessing more than 20 monosaccharide units). "Carbohydrate" is used in its usual annotation to denominate products of the formula  $C_x(H_2O)_y$ ,  
10 wherein x is 3 - 2,000, preferably 3 - 900, and wherein y is 3 - 2,000, preferably 3 - 900.

As long as they fulfil the requirements of the present invention, derivatives of said saccharides can also be employed as degeneration reducing agents.  
15 Derivatised saccharides are preferably selected from the group consisting of dehydrated saccharides, esterified saccharides, saccharides bearing one or more phosphate groups, one or more phosphonate groups, one or more phosphino groups, one or more sulfate groups, one or more sulfonate groups, and/or one or more amino groups. However, degeneration reducing agents  
20 comprising nitrogen are less preferred. Furthermore, the degeneration reducing agents preferably do not contain any  $CH_2$  or  $CH_3$  groups since the presence of such groups is known to result in the formation of undesired chloroform and/or other chlorinated organic compounds in electrolysis operations. More preferred derivatives of saccharides are selected from the group consisting of dehydrated  
25 saccharides and esterified saccharides.

Suitable monosaccharides are for example fructose, ribose, erythrose, and monoglyceraldehyde. Suitable oligosaccharides are for example lactose, maltose, and saccharose (also called sucrose). Suitable polysaccharides are  
30 amylose, cellulose. Saccharides which can be used according to the invention also include (partially) oxidised saccharides and derivatives thereof. An example of an oxidised saccharide that can be used is tartaric acid (D, L, meso,

and/or mixtures thereof). However, hydroxypolycarboxylic acids and especially meso tartaric acid are preferably not used. The (derivatised) saccharides can be in the open form or in the  $\alpha$ - or  $\beta$ -ring form. When the ring is open, the (derivatised) saccharide is a ketone or an aldehyde, generally referred to as a  
5 ketose and an aldose, respectively.

Examples of polycarboxylic acids which can be used include but are not limited to polymaleic acid, polyacrylic acid, Belsperse<sup>®</sup>, Belgard<sup>®</sup> EV, and Belgard<sup>®</sup> EV  
10 2000.

10

The one or more degeneration reducing agents can be dosed to the brine at any stage of the process, provided that the brine contains less than 1.5 g, preferably less than 1.0 g, more preferably less than 0.75 g, most preferably less than 0.5 g of dissolved active chlorine per litre of brine. In a most preferred  
15 embodiment, the brine to which the degeneration reducing agent(s) is/are dosed contains no active chlorine. In practice, this means that the degeneration reducing agent(s) is/are dosed to the brine after the dechlorination step, but before entrance of the brine feed into the electrolysis cells. This is to avoid early decomposition of the degeneration reducing agents due to reaction with said  
20 chlorine as much as possible. Dosing the degeneration reducing agents to the brine just after dechlorination, e.g. in the salt dissolver, is less preferred, since, preferably, the residence time of the degeneration reducing agents in the brine before it enters the electrolysis cells is made as brief as possible. Hence, preferably, the one or more degeneration reducing agents are dosed to the  
25 brine in a later stage of the process, e.g. after a primary brine treatment step. Most preferably, the degeneration reducing agents are dosed to the brine after said brine has been subjected to a purification step using an ion exchanger. It is also possible to dose the degeneration reducing agent(s) directly in the membrane electrolysis cells. However, since this will result in a flow change  
30 which may adversely affect the functioning of the membrane cell, this embodiment is less preferred.

It is to be understood that the word "dosing" is used to describe the step of adding the one or more degeneration reducing agents to the aqueous salt solution comprising sodium chloride which serves as feed brine for the membrane cell electrolysis process to produce chlorine in order to prevent degeneration of the membrane. This means that the complexing agent(s) is/are not already present in the sodium chloride compositions from which the brine is prepared. The dosing can be done continuously, meaning that for a certain period of time the compounds are continuously added to the feed brine. However, particularly if hold-up tanks which give the feed brine for the membrane a more constant composition are present in the process, it may be acceptable to dose the degeneration reducing agent intermittently during the operation, in which case the skilled person will be able to select the optimum interval times and optimum amounts of degeneration reducing agent(s) to be dosed by routine experimentation. A combination of these techniques is also possible. Examples of a combination of such techniques include, for instance, a process where the degeneration reducing compound(s) is/are first added continuously, then the addition is stopped, and then again it/they is/are added continuously. Furthermore, it is possible to dose the degeneration reducing agent in more than one stage of the process, for example, by dosing part of the degeneration reducing agent continuously or intermittently to the feed brine before the ion exchange purification step, while another part is dosed continuously or intermittently directly in the membrane cell.

The degeneration reducing agent(s) can be dosed to the feed brine in any conventional manner. Preferably, they are dosed to the feed brine in the form of an aqueous solution or as a solid.

The sodium chloride may be from any source but is preferably sodium chloride from a natural salt source such as rock salt, a subterranean sodium chloride deposit in a well exploited by means of dissolution mining, and/or solar salt, including lake or sea salt. The aqueous salt solution is prepared by dissolution of said salt source in water. For the water in the present process, any water

supply typically used in conventional chlor-alkali processes can be employed. It may for example be demineralised water, dechlorinated depleted brine, or mixtures thereof.

- 5 Preferably, the brine in the processes of the present invention comprises at least 100 g/l of sodium chloride, more preferably at least 150 g/l, even more preferably at least 200 g/l, and most preferably at least 300 g/l.

10 Preferably, brine leaving the electrolysis cells, also denoted as depleted brine, is first dechlorinated and subsequently recycled into the process. Before recycling to an electrolysis cell, the concentration of sodium chloride in the brine solution may be increased to obtain the most efficient operation of the cell. It is furthermore possible to store depleted brine in an anolyte tank where it is mixed with fresh, purified brine, after which it is returned to the electrolysis cells.

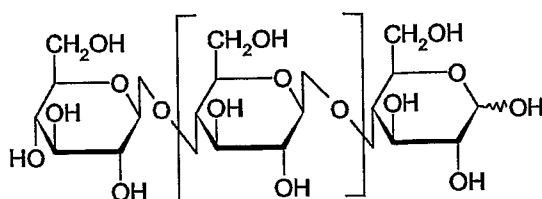
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Preferably, the concentration of the degeneration reducing agent(s) in the brine entering the electrolysis cells is kept at a constant level so that the composition of the brine for the membrane process is not fluctuating.

20 Typically, the total amount of degeneration reducing agents present in the feed brine entering the membrane electrolysis cell is, on average, less than 1,000 mg, preferably less than 500 mg per litre of feed brine. Preferably, less than 200 mg and more preferably less than 50 mg of degeneration reducing agent(s) is used per litre of feed brine. Concentrations of degeneration reducing agent(s) higher than 1,000 mg per litre of feed brine are also possible, but are less preferred. Typically, more than 0.1 mg, preferably more than 1 mg, and most  
25 preferably more than 5 mg of degeneration reducing agent(s) is used per litre of feed brine.

30 In a preferred embodiment of the present process to prepare chlorine from brine, besides the degeneration reducing agents, also one or more water-soluble cellulose ethers are used to reduce or inhibit fouling and/or clogging of the membranes.

Cellulose ethers are certain derivatives of cellulose. Cellulose is a polysaccharide composed of individual anhydroglucose units which are linked through a 1.4 glucosidic bond (see Formula A).



(Formula A)

The number "n" of anhydroglucose units in the polymer chain is defined as the degree of polymerisation (DP). The degree of polymerisation (DP) of cellulose depends on the origin of the cellulose. Preferably, the water-soluble cellulose ethers according to the present invention have a DP of between 250 and 30,000. Each anhydroglucose ring carries three OH-groups at positions 2, 3, and 6, which are chemically active. The distribution of the substituents introduced onto the polymer chain is largely determined by the relative reactivity of these three OH-groups.

Cellulose ethers are typically made by reacting some or all of these cellulose OH-groups of highly purified and bleached cellulose with one or more alkylating agents. Since potentially three hydroxyl groups are available on each anhydroglucose ring, derivatives of cellulose are usually characterised in terms of a "degree of substitution" (DS), which is an average per anhydroglucose unit for the whole chain and can range between 0 and 3. Reaction of merely one type of alkylating agent with cellulose results in a simple cellulose ether, whereas using of two or more types of alkylating agents leads to the formation of mixed ethers. The water-soluble cellulose ethers according to the present invention can be either simple or mixed ethers, preferably having a DS of between 0.2 and 3, more preferably between 0.5 and 2.5.

Cellulose ethers can be divided into ionic and non-ionic types. Ionic cellulose ethers, such as for example sodium carboxymethylcellulose, contain

substituents which are electrically charged. Nonionic cellulose ethers, such as methylcellulose and hydroxyethylcellulose, carry electrically neutral substituents. Mixed ethers with ionic and non-ionic substituents are classified according to their predominant features.

5

Cellulose ethers suitable for use according to the present invention can be either ionic or non-ionic cellulose ethers, as long as they are water-soluble. It is noted that by the term "water-soluble" is meant that the cellulose ether has a solubility in water at 20°C of at least 1 ppm, but preferably of at least 10 ppm,  
10 more preferably of at least 50 ppm, and most preferably of at least 100 ppm. Preferably, use is made of one or more cellulose ethers selected from the group consisting of alkyl, alkylhydroxyalkyl, hydroxyalkyl, and carboxyalkyl cellulose. More preferably, the cellulose ether according to the present invention is selected from the group consisting of carboxymethyl cellulose, sodium  
15 carboxymethyl cellulose, hydroxypropyl cellulose, hydroxyethyl cellulose, and hydrophobically modified hydroxyethyl cellulose. It was found that these types of cellulose ethers can be used in the process to prepare chlorine from brine, because in the presence of chlorine they will decompose into components that cause no worry in the chlor-alkali process. In particular, merely carbon dioxide,  
20 hydrochloric acid, and water are formed.

If water-soluble cellulose ethers are used, preferably their total amount present in the brine feed is less than 500 mg, more preferably less than 250 mg per litre of the brine feed. If water-soluble cellulose ethers are used, preferably their total  
25 amount is at least 1 mg, more preferably at least 5 mg, and most preferably at least 25 mg per litre of the brine feed.

It is noted that the term membrane as used throughout this specification is meant to denote any membrane conventionally employed in an electrolysis cell.  
30 Examples of frequently used membrane types in electrolysis cells are Nafion® ex DuPont and Aciplex® ex Asahi Kasei Corporation.



The present invention is elucidated by means of the following non-limiting Example.

## 5 **Example**

### *Equipment:*

A membrane electrolysis experiment was executed in a laboratory set-up consisting of the following equipment:

- 10     • 2 cylindrical glass containers, *i.e.* the anolyte vessel and the catholyte vessel, with an effective volume of about 125 ml each.
- A 5 cm, 1 cm diameter glass connection between the containers equipped with a construction to place a 2.2 cm effective diameter electrolysis membrane in the tubing separating the anolyte from the
- 15     catholyte.
- 1 reference electrode placed as close as possible to the membrane surface in the catholyte and 1 reference electrode placed as close as possible to the membrane surface in the anolyte. These electrodes are used to measure the voltage drop over the membrane.
- 20     • Two magnetic stirring devices to stir the catholyte and anolyte vessels.
- A thermostat bath to control the process temperature at a constant value of 50°C.
- A Pt anode and a Pt cathode, each placed in the corresponding cylindrical glass container.
- 25     • A rectifier connected to the Pt electrodes so that the electrolysis equipment can be operated at a selected constant current.

A schematic picture of this laboratory set-up is depicted in Figure 1, wherein A represents the reference electrodes, B the Pt-electrodes, C the membrane, and D the electrolyte solutions.

30

### *Process fluids:*

A stock solution of 5 litres of nearly saturated brine (300 g/l of NaCl) was prepared by adding sodium chloride (ultrapure grade ex Merck) to distilled water. The saturated brine was filtered over an IOX-type cation resin exchanger at pH=10 at 75°C to remove any traces of polyvalent cations. Subsequently,  
5 100 ppm (mg/l) of Fe were added to the solution as FeCl<sub>3</sub>. The resulting brine is called the iron-containing electrolysis feed brine.

A stock solution of 5 litres of caustic with a concentration of 21 wt% of NaOH was prepared by dissolving ultrapure NaOH (ex Merck) in distilled water.

#### 10 *Experimental*

125 ml of the iron-containing feed brine were added to the anolyte vessel and 125 ml of the above-described caustic solution were added to the catholyte vessel. Both the catholyte and anolyte vessels were stirred using the magnetic stirrer and the process temperature was kept at 50°C using the thermostat  
15 batch. The anode and the cathode were connected to the rectifier and the electrodes for measuring the voltage drop over the membrane were connected to a Volt meter. About 5 minutes after starting the experiment, the temperature in both anolyte and catholyte was 50°C and 5.0 g of saccharose were added to the anolyte. About 1 minute later, the saccharose had dissolved completely.  
20 Subsequently, a constant current through the membrane of 1.5 A was realised using the rectifier. Every 10 minutes, the pH of the anolyte was adjusted to pH=1.3 by the dosing of a few drops of concentrated caustic solution.

The load averaged resistance of the membrane was measured over time by measuring the I [Ampere] – V [Volt] curve from 0.25 A to 2.0 A with steps of  
25 0.25 A. Each time a curve was measured, the current through the membrane was set to 1.5 A again.

Subsequently, the anolyte was removed from the corresponding vessels using a vacuum suction device. Special attention was paid to keeping all electrodes at  
30 exactly the same position. Subsequently, the anolyte container was filled with iron-containing electrolysis brine. The anolyte removal and filling step was

executed 3 times in order to ensure that any traces of saccharose were effectively removed from the anolyte container. As soon as the anolyte temperature was 50°C again, the pH of the anolyte was adjusted to pH=1.3 by adding a few drops of 6M ultrapure hydrochloric acid to the anolyte. The experiment was continued by realising a constant current of 1.5 A through the membrane.

In Table 1, the results of the experiment are shown.

10

Table 1

Saccharose present	Time / min	R / Ohm · cm <sup>2</sup> (average)
Yes	1	1.87
Yes	5	1.89
Yes	12	1.95
Yes	20	1.90
Yes	30	1.86
Yes	46	1.91
Yes	62	1.92
Yes	82	1.91
No	2	2.04

During the experiment, it was observed that in the presence of saccharose the membrane was coloured light brown. After continuing the experiment in the absence of saccharose, the colour of the membrane clearly changed from light brown to dark brown within a few minutes. As can be seen in the table, the load averaged current is stable and does not significantly change during the experiment in the presence of sugar. Continuation of the experiment in the absence of sugar results in an increase of the load averaged membrane resistance from 1.91 Ohm·cm<sup>2</sup> to 2.04 Ohm·cm<sup>2</sup>, which indicates rapid membrane fouling.

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**CLAIMS**

1. Membrane cell electrolysis process to prepare chlorine from an aqueous salt solution comprising sodium chloride comprising the steps of
- 5
- dissolving a sodium chloride source in water to form an aqueous salt solution comprising sodium chloride, and
  - dosing one or more degeneration reducing agents selected from the group consisting of monosaccharides, oligosaccharides, poly-

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  - saccharides, polycarboxylic acids, polyacrylates, polymaleic acids, and derivatives thereof to said aqueous salt solution in a total amount of, on average, between 0.1 mg and 1,000 mg per litre of aqueous salt solution at a stage of the electrolysis process where the amount of active chlorine dissolved in said aqueous salt solution is less than

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  - 1.5 g per litre of aqueous salt solution and/or to the membrane cells, in order to reduce fouling and/or clogging of the membrane in said membrane cell.
2. Process according to claim 1 wherein the degeneration reducing agent(s)
- 20
- is/are dosed to the aqueous salt solution after it has been treated with an ion exchanger for purification and before it enters the membrane cell.
3. Process according to either of the preceding claims wherein the total amount of degeneration reducing agents in the aqueous salt solution upon
- 25
- entrance into the electrolysis cells is, on average, less than 50 mg per litre and more than 5 mg per litre of aqueous salt solution.
4. Process according to any one of the preceding claims wherein the
- 30
- degeneration reducing agent is selected from the group consisting of lactose, maltose, saccharose, amylose, and cellulose.

5. Process according to any one of the preceding claims wherein one or more water-soluble cellulose ethers are also present in the aqueous salt solution.
- 5 6. Process according to claim 5 wherein the water-soluble cellulose ether is selected from the group consisting of carboxymethyl cellulose, sodium carboxymethyl cellulose, hydroxypropyl cellulose, hydroxyethyl cellulose, and hydrophobically modified hydroxyethyl cellulose.
- 10 7. Process according to claim 5 or 6 wherein the total amount of water-soluble cellulose ethers in the aqueous salt solution upon entrance into the membrane cell is, on average, less than 500 mg per litre and more than 1 mg per litre thereof.
- 15 8. Use of one or more degeneration reducing agents selected from the group consisting of monosaccharides, oligosaccharides, polysaccharides, polycarboxylic acids, polyacrylates, polymaleic acids, and derivatives thereof, to reduce or inhibit fouling and/or clogging of a membrane used in a membrane cell electrolysis process to prepare chlorine from an aqueous salt solution comprising sodium chloride, wherein said degeneration reducing agent(s) is/are present in the aqueous salt solution which is present inside the membrane cell.
- 20
9. Use according to claim 8 wherein the degeneration reducing agent is present in a total amount of between 0.1 and 500 mg per litre of aqueous salt solution.
- 25

10. Use according to claim 8 or 9 wherein also one or more water-soluble cellulose ethers selected from the group consisting of carboxymethyl cellulose, sodium carboxymethyl cellulose, hydroxypropyl cellulose, hydroxyethyl cellulose, and hydrophobically modified hydroxyethyl cellulose is present per litre of aqueous salt solution in a total amount of between 1 and 500 mg.

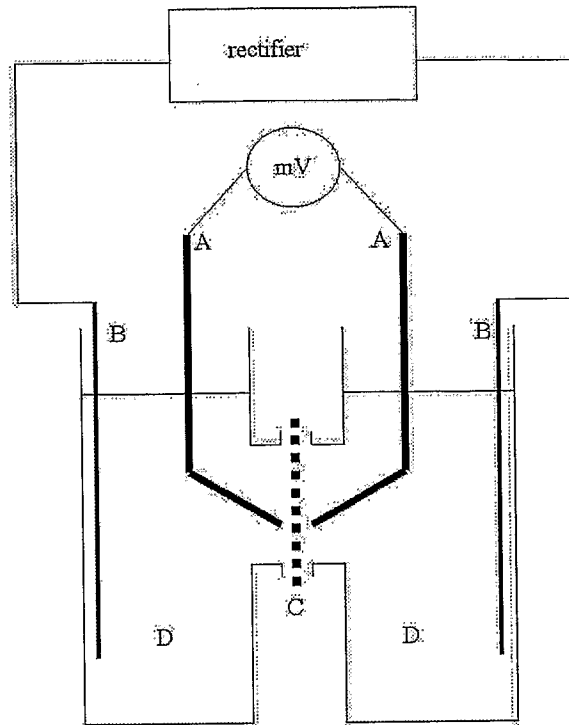


Figure 1