



(51) International Patent Classification:
C02F 1/461 (2006.01)

(21) International Application Number:
PCT/EP2009/065077

(22) International Filing Date:
12 November 2009 (12.11.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
BO2008A000688 13 November 2008 (13.11.2008) IT

(71) Applicant (for all designated States except US): GIMA S.P.A. [IT/IT]; Via Kennedy, 17, I-40069 Zola Predosa (BO) (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): QUADRELLI, Sandro [IT/IT]; Via San Pancrazio, 86, I-40069 Zola Predosa (BO) (IT). FERRO, Sergio [IT/IT]; Via dei Cedri, 26, I-44123 Ferrara (IT).

(74) Agent: NEGRINI, Elena; c/o. AGAZZANI & ASSO-CIATI S.R.L., Via dell'Angelo Custode 11/6, I-40141 Bologna (IT).

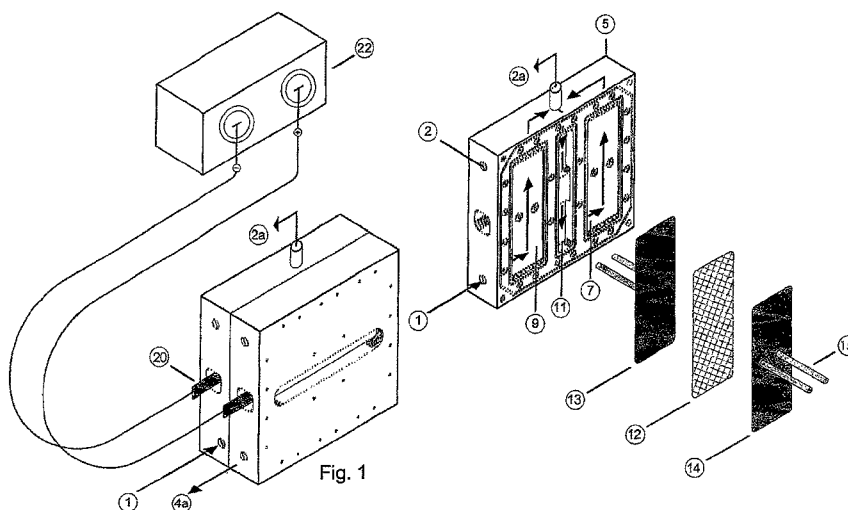
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: ELECTROCHEMICAL REACTOR



(57) Abstract: An electrochemical reactor comprises at least one electrolytic cell, each cell is divided by a membrane (12) into two electrode chambers (7, 8), each one is crossed by flows of liquid and each having at least a corresponding electrode (13, 14). Both the electrodes (13, 14) have one own face directly in contact with the membrane (12) and have a plurality of openings (21) for the passage of the liquid. Each electrode (13, 14) is provided with one or more contact means (15) for the power supply.

WO 2010/055108 A1

ELECTROCHEMICAL REACTOR

TECHNICAL FIELD

5 The present invention concerns an electrochemical reactor for the electrochemical activation of water and, in particular, for the electrolytic treatment of aqueous solutions containing halides, for producing neutral solutions (or with a nearly neutral pH, i.e. between 6.0 and 7.5) to be used as disinfectants and/or sterilizing agents.

10 BACKGROUND OF THE INVENTION

The electrolytic treatment of weakly saline waters (otherwise known as "diluted brines", because the dissolved salts are a few grams per liter) is a process described in the literature with the term "electrochemical activation of water". In order to carry out the
15 electrochemical process, the reactor size must be appropriately chosen; in particular, in consideration of the high resistivity of diluted electrolyte solutions, the inter-electrode distance has to be maintained at properly low values, so as to limit the ohmic drop and thus the potential difference applied to the electrodes.

20 As an example, one can consider the Russian-designed tubular cells described in EP 0842122 B1 (Bakhir and Zadorozhny): they have a very small inter-electrode distance (about 3 mm) and are equipped with a ceramic separator, which is quite fragile and delicate (its wall thickness is less than 1 mm), representing also a constraint for the reactor size (and hence for its productivity). Flowing through the aqueous solution,
25 current lines are perpendicular to both the electrode surfaces and the diaphragm; in addition, given the cylindrical geometry of the system, the current lines have also a radial distribution. Other examples of cells for the electrochemical activation of water should be considered structural variations of the previous one; possible examples are those reported in EP 0922788 B1 (Naida and Pushnyakov), or in GB 2449735 A
30 (Iltsenko and Naida): in both cases, the reactor maintains the above cylindrical geometry, as well as the ceramic diaphragm to separate the electrode compartments.

Moving to the field of chlor-alkali industrial cells, electrode structures in direct contact with the separator (either a diaphragm or a membrane), the latter being placed between the two electrode compartments, are known. As an example, a membrane-type electrolytic cell is described in WO 85/02419 (Johnson): two porous electrodes
5 (permeable to both the electrolyte solution and the gas produced by the electrolytic process) are pressed against the membrane to form a so-called "zero-gap structure", i.e. an intimate contact between adjacent components, which can anyway be disassembled at request. In chlor-alkali synthesis, cells of this type are usually fed with brines close to saturation concentrations (250-300 g/l NaCl).

10

As discussed, for example, in US 7141147 B2 (Shimamune) and in EP 1577424 A1 (Houda and Noaki), a proper zero-gap configuration requires also the presence of suitably flexible means, aimed at maintaining a predetermined pressure between the electrode elements and the membrane interposed between them; generally, said elastic
15 element represents a portion of the cathode device itself, which is thus made up of several layers.

20

A quite advanced electrochemical reactor, for the treatment of diluted brines, is described in EP 1969159 B1 (Bohnstedt et al.): it comprises two cells equipped with
20 planar electrodes in separated compartments, the presence of a separator preventing that what produced at the anodes could be reduced at the cathodes (with obvious decreases for the yield of the electrochemical synthesis).

25

The reactor design allows the diluted brine to be initially subjected to the cathodic treatment and subsequently to the anodic one, with the result that the outgoing solution contains oxidizing ("active") chemical species and has a pH close to neutrality (usually in the range between 6.5 and 7.5).

30

Despite the engineering solution described in EP 1969159 B1 represents a significant improvement, compared to what was previously proposed by technology, there remain some issues, particularly detectable in the following points:

- the thin membrane that separates each anode chamber from the cathode one requires the use of appropriate spacers, which support the membrane while maintaining a distance from the latter and the electrode surfaces; since these spacers are immersed in the electrolyte solutions, experiencing their chemical aggression, they are progressively deteriorated and require to be regularly substituted;
- even though the distance between electrodes (anode and cathode, in their respective chambers) is relatively low, the resistivity of diluted electrolyte solutions is anyway responsible for significant ohmic drops, which result in energy costs and in the need to adopt appropriately oversized current generators;
- since the heat produced by Joule effect is proportional to the resistivity of the medium interposed between the electrode surfaces, the problem described in the preceding paragraph shall also determine significant heating effects for both the solution and the electrodes, with possible consequences on the process yield as well as on the service life of the different components of the device.

DISCLOSURE OF THE INVENTION

An object of the present invention is to overcome the limitations described above and in the known technique, making available a reactor comprising electrolytic cells, suitable for the electrochemical activation of diluted brines, with no spacers between the membranes and the electrode surfaces.

A second object of the present invention is to provide an engineering solution that minimizes the Joule effect due to current flow, resulting in an improved process yield and reduced risks of unwanted side reactions (such as the synthesis of chlorites, chlorates or perchlorates, as a result of the treatment of chloride-containing solutions).

Under a further aspect, it is an object of the present invention to make available an electrochemical reactor capable of producing electrochemically activated solutions having a pH close to neutrality, being powered with potential differences significantly lower than those required by the state of the art.

The present invention relates to a reactor comprising three inner rooms, consisting of an expansion chamber and two electrolytic cells, obtained within a single structure; outwardly, this structure looks like a box-shaped parallelepiped, formed by two halves
5 that are assembled to form a coherent whole. Within said structure, the liquid flow is adjusted so that there is an initial, single passage within the cathode chambers (the incoming liquid is distributed between them), and a subsequent anodic treatment in the two anode rooms, which are passed through in sequence. Leaving the cathode chambers, and prior to the anodic processes, the liquid flows through the intermediate
10 expansion chamber, in which a separation between the liquid and the gas produced during the cathodic process takes place.

As briefly described in the examination of the state of the art, the electrolytic reactors for the synthesis of electrochemically activated water are usually characterized by an
15 inter-electrode distance of a few millimeters as well as by the presence of a ceramic diaphragm arranged between these electrodes, at an appropriate distance from them. The authors of the present invention have found a way to obtain similar results even with significantly lower inter-electrode distances, and with the use of cation-exchange polymeric membranes (replacing the ceramic diaphragm), provided that the chosen
20 electrodes and membrane have appropriate characteristics.

Through a series of tests, the authors of the present invention have verified the feasibility of using zero-gap structures within a reactor for the electrochemical activation of water, and how it allows an efficient synthesis of electrochemically
25 activated solutions, while solving a number of drawbacks.

It would be reasonable to assume that the use of a zero-gap structure within an electrochemical cell for the electrochemical activation of water were counterproductive: actually, the inter-electrode distance must be kept at values not too high but, conversely,
30 an over-minimization of that distance may lead to a corresponding reduction in cell potential, with consequent negative effects on the electrochemical activation process. Therefore, it has to be regarded as unexpected the result reached by the authors of the

present invention, who identified the way to overcome the prejudices of the state of the art.

BRIEF DESCRIPTION OF THE DRAWINGS

5

The description of the present invention will be more understandable while referring to the attached drawings:

- 10 - Figure 1 illustrates an isometric view of the electrochemical reactor, object of this invention, in which also a power generator is drawn;
- Figure 2 is an exploded view of the reactor illustrated in Figure 1, showing details of the two halves of the reactor; in this figure, electrodes are represented in a purely schematic form;
- Figures 3 and 4 are views of the inner faces of the two halves of the reactor;
- 15 - Figures 5 and 6 are sectional views according to plan traces A-A' and B-B' shown in Figure 3;
- Figure 7 illustrates a partial and enlarged view of a detail of Figure 6;
- Figure 8 shows an enlarged, detailed isometric view of any of the electrodes of Figure 2, used for carrying out the present invention.

20

BEST MODE OF CARRYING OUT THE INVENTION

The electrochemical reactor object of the present invention is shown in assembled form in Figure 1. That reactor is equipped with three internal cavities, produced in the bodies
25 **5** and **6** of the reactor, as shown in Figure 2; each lateral cavity represents an electrochemical cell, which is divided by a membrane **12** in two faced chambers **7 - 8, 9, 10**, each crossed by liquid flows and each equipped with at least one respective electrode **13** (at the cathode side, in the body **5** of the reactor) and **14** (at the anode side, in the body **6** of the reactor) having a flat face directly in contact with the membrane **12**.
30 Each electrode **13, 14** has a plurality of openings **21** that allow the passage of the liquid: these openings **21** consist of holes through the thickness of that electrode **13, 14**; preferably, the openings **21** are regularly distributed, as a matrix, over the entire surface

of the electrode **13, 14**. More specifically, each electrode **13, 14** can be obtained from a network or a stretched and flattened metal sheet; the openings **21** may have different forms: in general, they are diamond-shaped with axes size between 0.3 and 5 mm, and more preferably between 1 and 3 mm. The electrode main surfaces are flat and mutually
5 parallel, and the face in contact with the membrane is preferably free of protrusions or bumps that might damage the membrane itself.

The electrodes **13, 14** are made of an electrically conducting material, metal, metal alloy or glassy carbon; it is preferable to use either titanium (pure or containing any impurity)
10 or a metal alloy in which titanium is the major component; other valve metals can be considered (such as tantalum, zirconium or niobium), as well as nickel, copper or stainless steel. The electrically conductive substrate can then be coated with a suitable catalyst, and this applies in particular for the electrode that will be housed in the anode compartment of each electrochemical cell. Suitable catalysts are those noble metals of
15 the platinum family (Ir, Ru, Os, Rh, Pd, Pt), their oxides, either pure or blended with other oxides, and particularly with valve metal oxides as well as oxides of titanium and tin.

Each electrode **13, 14** has a thickness of between 0.1 and 4 mm, and preferably between
20 1 and 2 mm; it is also provided with one or more contact means **15** for the electric connection to a power supply.

Each electrode **13, 14** is then shaped as a net or a perforated plate, and has one own flat face directly in contact with a membrane **12**; the latter divides the internal cavity into
25 two electrode chambers **7, 8; 9, 10**, in which the electrodes **13, 14** are housed: the liquid to be electrochemically treated flows in rooms **7, 8, 9** and **10** and laps the face of the electrode **13, 14** opposite to that in direct contact with the membrane **12**, arriving also to wet the membrane itself, through the openings **21** present on the electrode **13, 14**.

Each electrode chamber **7, 8, 9, 10** is provided with lateral seats **18** to accommodate
30 lateral side edge portions of the respective electrode **13, 14**; these seats **18** of the chamber **7, 8, 9, 10** laterally delimit the passage **19**, which has a shape in plan similar to

that of the electrode. The passage **19** permits the flow of the liquid entering and leaving the chamber **7, 8, 9, 10** through inflow **16** and outflow ducts **16a** present in the chamber itself; the width of the passage is sufficient for the liquid to pass with little resistance and is somewhat lower than the other dimensions of the passage itself. In particular, the chamber **7, 8, 9, 10** has the appearance of a flattened parallelepiped, with a depth
5 between 0.2 and 9 mm and preferably between 1 and 5 mm; the width of the passage **19** is between 0.1 and 5 mm, and preferably between 0.5 and 3 mm.

From the above description, it follows that the depth of each electrode chamber **7, 8, 9, 10**, corresponding to the combined thickness of the electrode with the width of the
10 passage for the liquid, is between 0.2 and 9 mm, where the electrode thickness **13, 14** is between 0.1 and 4 mm, and the thickness of the passage for the liquid **19** is between 0.1 and 5 mm. The depth of each electrode chamber **7, 8, 9, 10** is preferably between 1 and 5 mm, and the ratio between the width of the passage for the liquid **19** and the thickness
15 of the electrode **13, 14** is preferably between 0.5 and 2.

Finally, each chamber **7, 8, 9, 10** contains one or more supporting means **18** intended for touching the electrode **13, 14** while supporting it.

The membrane **12** is shaped in form of sheet or film, usually in polymeric organic
20 material, possibly halogenated, or composite (organic/inorganic), and is provided with active groups such as carboxyl, sulfonic or amine groups; said polymeric membranes can have a single layer or multiple layers, and may contain reinforcing plastic gratings, often TeflonTM-based. Among the different polymeric membranes that can be used, examples are those produced by DuPont (known as NafionTM), Asahi Glass (FlemionTM)
25 and Fumatech (FumapemTM and FumasepTM). The edge of that membrane is tightly sealed between the two bodies **5** and **6** of the reactor.

Each of the above-mentioned supporting means **18** consists in a branch or rib, for example straight, obtained in the respective body **5** or **6**, protruding in the chamber and
30 longitudinally crossing all or part of the passage **19**, touching the electrode **13, 14** in its face opposite to the membrane **12**, so that he could not leave or bend over from its correct position of total contact with the membrane **12**.

The membrane **12** is tightened between two flat, facing and opposing electrodes **13** and **14**, each one in direct contact with a respective side of said membrane **12**, and the membrane portion tightened between the electrodes is coplanar with the membrane edge
5 tightened between the two bodies **5** and **6** of the reactor: in this way, the membrane is not subjected to any particular stress, is well protected and almost insensitive to vibration or shock, as well as to any difference in pressure that could create in the electrode chambers during the reactor functioning.

10 The inlet and outlet ducts for fluids **1**, **2**, **3**, **4** and **4a**, as well as that for venting the produced gases **2a**, are obtained, at least in part, in the bodies **5** and **6** of the reactor.

Each contact means **15** is orthogonal to the plane of the respective electrode **13**, **14** faces and exits the chamber **7**, **8**, **9**, **10** through a hole **17** obtained in a body **5** or **6** of the
15 reactor, to allow electrical connection to a connection means **20**, having for example the form of a bar or rod with holes for coupling with the electrical contacts. Said connection means **20** may be sliding pushed in a respective location, obtained in the reactor body **5** or **6**, where the holes **17** for the passage of the contact means **15** are located.

20 Each contact means **15** also includes a threaded portion that can be mated with threaded nut means for connecting to the connection means **20**; the latter is thus provided with connections for different contact means **15**, for at least two electrodes, as well as for the electrical wiring connection to the polarity of an electric source **22**.

25 The portion of the seat for the electrical connection means **20** opposite to the holes **17** for the contact means **15** is open to the outside through a buttonhole, to allow the screwing of the threaded nuts to the threaded portions of the contact means **15**. The contact of the electrical connection means **20** for connecting the electrical wires is preferably obtained on one end of the same electrical connection means **20**, which
30 protrudes from the body of the reactor.

The innovative aspects of the present invention will be made more evident considering the conditions of use of the reactor, while referring in particular to Figures 2 and 7.

As discussed by Vitold Bakhir for example in "Theoretical aspects of the electrochemical activation" (Summaries of papers and brief reports - Second International Symposium on Electrochemical Activation in Medicine, Agriculture and Industry, Moscow 1999), the effects of electrochemical activation of water are more marked and persistent, the lower the degree of mineralization of the treated water. Considering the relaxation phenomena that restore the water conditions as they were before the electrochemical activation, the most significant changes occur when the treated water has a mineral content between 0.1 and 1 g/l. The magnitude of these changes decreases if the degree of mineralization is either reduced from 0.1 g/l to zero, or increased from 1 to 5 g/l; for a mineralization content exceeding 5 g/l, changes related to the relaxation phenomena become progressively less evident, disappearing at all if the mineral content increases to approximately 100 g/l. Thus, in order to maximize the effects of the electrochemical activation while minimizing the energy expenditure required for the attainment of such activation, it is convenient to consider solutions containing a few grams per liter of dissolved salts, preferably less than 10 g/l and more preferably around 5 g/l.

20

Drinking water typically, and mostly, contains chloride ions and sodium ions; other chemical species may be sulfates, carbonates, calcium and magnesium ions; to a minor extent, also iron and nitrate ions can be found, as well as dissolved gases including oxygen and nitrogen. In order to prepare an electrochemically activated solution, to be used as a disinfectant or sterilizing agent, it is particularly advisable to use softened or demineralized water, to which an alkali metal halide, such as sodium chloride or chloride potassium, is added in amounts from 1 to 10 g/l, and preferably in amounts between 3 and 6 g/l. In what follows, said solution will be referred to as diluted brine.

25

The diluted brine entering the reactor first passes through the cathode compartments **7** and **9**, by distributing itself between the two chambers by means of the apposite conduct **1** obtained within the body **5** of the reactor; subsequently, the solution reaches the anode

30

compartments **8** and **10**, which are crossed in sequence (the liquid distribution that takes place at the cathode side is not reproduced at the anode side). With reference to Figures 2 and 7, the liquid flows through the passage **19** of a cathode chamber **7, 9** on one side of the membrane **12**, lapping the cathode **13** and also wetting the membrane **12** through the openings **21** present on the electrode **13**. The fluid leaving the chamber **7, 9** passes across the intermediate expansion chamber (obtained in the body of the reactor by the coupling of the two half-rooms **11**, in which the gas produced by the cathodic process are separated from the liquid and discharged, together with a part of the liquid, through the outlet tap **2a** placed on the top of the body **5** of the reactor. Through a proper regulation of the outgoing fluid volume, it is possible to adjust the pH of the electrochemically activated solution produced by the reactor itself; said pH is preferably between 6.0 and 7.5. Subsequently, the fluid leaves the expansion chamber through the conduit **4** and reaches the first anode chamber **8**, in which a first anode **14** is located. The solution flows alongside the anode **14** and, for the presence of the holes **21** present on the electrode, is also able to wet the membrane **12**. The dynamics of the processes that take place in rooms **7, 9** and **8** are similar, the only difference being that the two electrodes **13** and **14**, in contact with opposite sides of the membrane **12**, are polarized in the opposite way, one being the cathode (negative polarity) and the other being the anode (positive polarity). Finally, the liquid that comes out of the first anode chamber **8** through the drainage holes **16a**, passes across the duct **3** and enters the second anodic chamber **10**, prior to leave the reactor through the outlet duct **4a**.

By focusing on one or the other electrode chambers of the cell portion shown in Figure 7, it is easy to recognize the membrane **12**, the electrode **13, 14** in contact with it through one of its surfaces and that points the other surface toward the passage **19**, which is delimited by the electrode surface and the bottom of the chamber (body **5** or **6** of the reactor).

Since the diluted brine penetrates with difficulty between the electrode and the membrane, the electrode surface directly in contact with the membrane is unable to operate well: as a result, the electrochemical reaction takes place preferentially on the electrode surface pointed toward the passage **19**, where the liquid flows, and the current

lines between that face and the corresponding electrode face on the other side of the membrane does not take a straight course but circular, penetrating through the holes **21** present on the electrodes **13, 14**. In consideration of that, the catalytic layer that coats the electrodes **13, 14** may well cover both the sides of the same (acting as a protective
5 coating against a chemical or electrochemical corrosion of the conductive substrate) but will have to be especially localized on each electrode face opposed to the one in direct contact with the membrane **12**. The inter-electrode space is then equal to the sum of the thicknesses of the two electrodes on both sides of the membrane plus the thickness of the membrane itself. As previously mentioned, in order for the cell voltage to remain
10 within acceptable values, the thickness of each electrode **13, 14** should preferably be selected from 1 to 2 mm.

In addition, the authors of the present invention have highlighted that also the membrane plays an important role: in particular, it acts as an ion exchanger (mostly
15 protons and sodium cations, in the case of a diluted sodium halide brine). Without wishing to bind to any particular theory, it is reasonable to assume that the solution at the cathode side is enriched with hydroxyl anions, which are generated due to water reduction: if the membrane is sufficiently thin and permeable to other ionic species (in addition to cations), the hydroxyl anions can cross the membrane, attracted by the
20 electric field, and discharge on the anode, producing oxygen. This is a phenomenon against which precautions should be taken, in order to limit it, since the discharge of hydroxyl anions can depolarize the anode, preventing or limiting the formation of the active species of interest. It is therefore preferable to choose a membrane with a thickness ≥ 150 microns, and with proper physico-chemical characteristics; in tests
25 performed in the laboratory, the NafionTM membrane produced by DuPont showed to be particularly convenient and performing.

The functioning of the reactor object of the present invention will now be presented through some examples; by way of comparison, a first comparative example based on
30 the use of the reactor described in EP 1969159 B1 is reported too.

EXAMPLE 1.

The electrolytic reactor described in EP 1969159 B1 (equipped with DSA[®] electrodes produced by DeNora at the anode side, with Hastelloy 22 stainless steel electrodes at the cathode side and with Fumapem[™] membranes by Fumatech, with a 60 microns thickness) was fed with a diluted brine containing about 4.5 g/l NaCl (conductivity of the brine: about 6.5 mS/cm), at a flow rate of 80 l/h. By setting a potential difference of 18 V between the electrical connection means, a current of 85 A was measured. The solution exiting from the reactor had a pH of 7.1, a redox potential equal to +800 mV_{SCE} (measured by a platinum wire against a Saturated Calomel Electrode, as indicated by the initials SCE) and an oxidizing substances content (determined by iodometric titration and expressed as "active chlorine") equal to 200 mg/l. It was also pointed out that the solution had a temperature of about 36 °C, nearly 10 degrees higher than the inflowing solution (which temperature was around 26.5 °C).

15

EXAMPLE 2.

The reactor object of the present invention (equipped with titanium mesh electrodes – obtained from a stretched and flattened sheet of Ti – covered with a catalytic layer containing IrO₂ and RuO₂ at the anode side, with titanium mesh electrodes covered with a platinum-containing catalytic coating at the cathode side, and Fumapem[™] membranes by Fumatech between these electrodes) was fed with a diluted brine containing about 5 g/l NaCl (conductivity of the brine: about 7.5 mS/cm), at a flow rate of 90 l/h. By setting a potential difference of 7.5 V between the electrical connection means, a current of 90 A was measured. The solution exiting from the reactor had a pH of 7.2, a redox potential amounting to +865 mV_{SCE} and an oxidizing substances content (determined by iodometric titration and expressed as "active chlorine") equal to 170 mg/l.

25

EXAMPLE 3.

30

The reactor of the example 2 was opened and the Fumapem[™] membranes by Fumatech were replaced with Nafion[™] membranes produced by DuPont (thickness: about 250

microns); furthermore, the cathodes with the platinum-based catalytic coating were replaced with two titanium mesh electrodes without any catalytic layer. Once the reactor was reassembled, it was fed with a diluted brine containing about 4.5 g/l NaCl (conductivity of the brine: about 6.5 mS/cm), at a flow rate of 90 l/h. By setting a potential difference of 9 V between the electrical connection means, a current of 72 A was measured. The solution exiting from the reactor had a pH of 7.2, a redox potential amounting to +870 mV_{SCE} and an oxidizing substances content (determined by iodometric titration and expressed as "active chlorine") equal to 230 mg/l.

10 EXAMPLE 4.

The reactor of the example 3 was fed with a diluted brine containing about 5.5 g/l NaCl (conductivity of the brine: about 8.4 mS/cm), at a flow rate of 110 l/h. By setting a potential difference of 9 V between the electrical connection means, a current of 77 A was measured. The solution exiting from the reactor had a pH of 7.2, a redox potential amounting to +870 mV_{SCE} and an oxidizing substances content (determined by iodometric titration and expressed as "active chlorine") equal to 265 mg/l.

20 EXAMPLE 5.

The reactor of the example 3 was fed with a diluted brine containing about 4.5 g/l NaCl (conductivity of the brine: about 6.5 mS/cm), at a flow rate of 130 l/h. By setting a potential difference of 12 V between the electrical connection means, a current of 110 A was measured. The solution exiting from the reactor had a pH of 7.3, a redox potential amounting to +810 mV_{SCE} and an oxidizing substances content (determined by iodometric titration and expressed as "active chlorine") equal to 220 mg/l. During this test, a slight increase in temperature of the outflowing solution was found (+6 degrees: inflowing solution at 17 °C, outflowing solution at 23 °C); using a special probe, the temperatures of the two cathodes were monitored, through their respective current connection means, resulting in about 40 and about 50 °C (the electrode closest to the inflowing solution inlet had the lowest temperature).

EXAMPLE 6.

The reactor of the example 3 was fed with a diluted brine containing about 4.5 g/l NaCl (conductivity of the brine: about 6.5 mS/cm), at a flow rate of 110 l/h. By setting a potential difference of 9 V between the electrical connection means, a current of 48 A
5 was measured. The solution exiting from the reactor had a pH of 7.2, a redox potential amounting to +780 mV_{SCE} and an oxidizing substances content (determined by iodometric titration and expressed as "active chlorine") equal to 225 mg/l. The temperatures of the two cathodes were monitored, through their respective current
10 connection means, resulted to be 22.4 and 26 °C (the electrode closest to the inflowing solution inlet had the lowest temperature).

CLAIMS

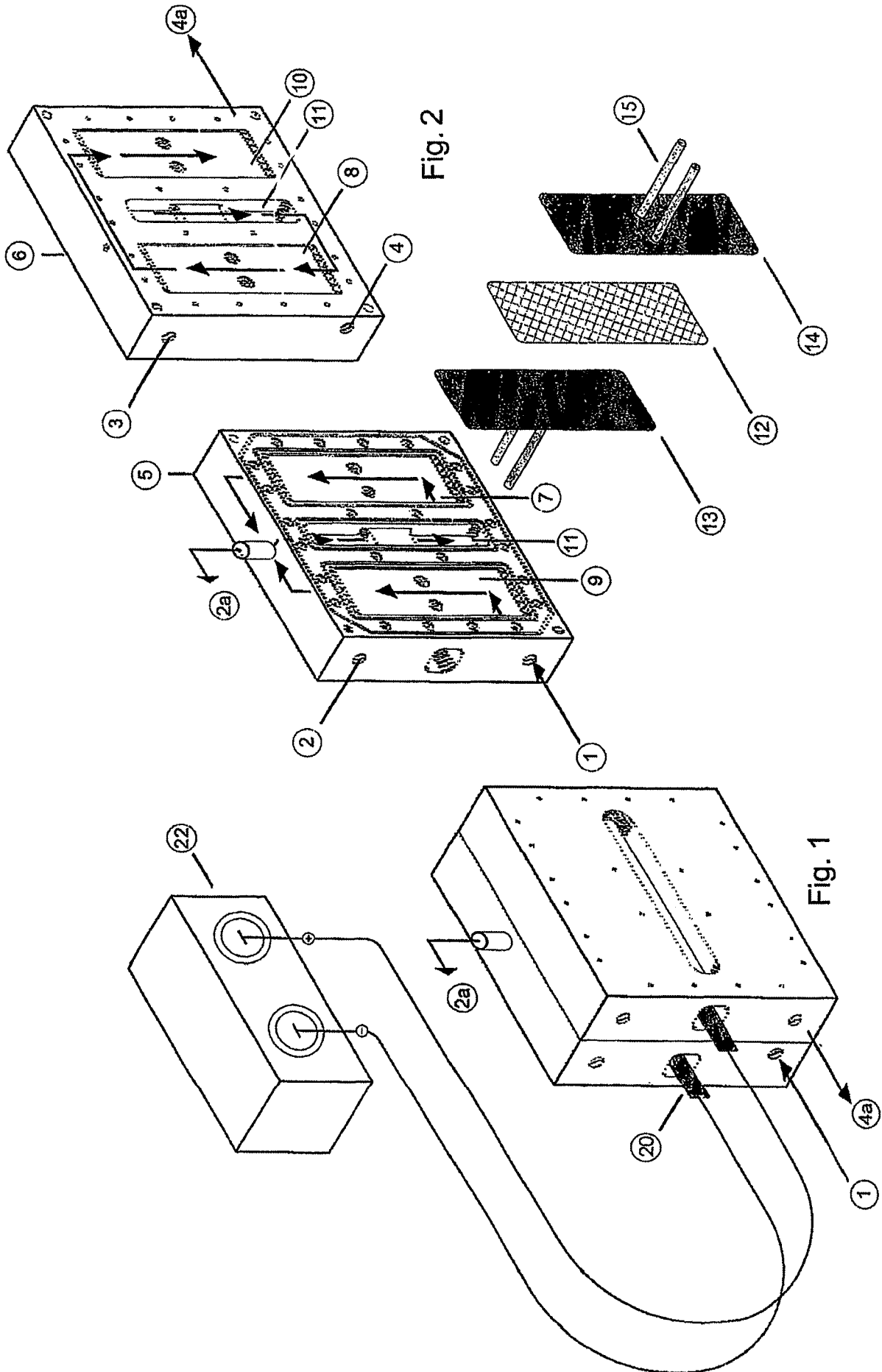
- 1) Electrochemical reactor comprising at least one electrolytic cell, each cell being divided by a membrane (12) into two electrode chambers (7, 8), each one crossed
5 by flows of liquid and each having at least a corresponding electrode (13, 14); said cell being characterized by the fact that:
- both the electrodes (13, 14) have one own face directly in contact with the membrane (12) and have a plurality of openings (21) for the passage of the liquid;
 - 10 - each electrode (13, 14) is provided with one or more contact means (15) for the power supply.
- 2) Reactor according to claim 1 characterized by the fact that it is equipped with three internal chambers, constituted by an expansion chamber and two electrolytic
15 cells.
- 3) Reactor according to claim 1 or claim 2 and characterized by the fact that the depth of each electrode chamber (7, 8, 9, 10), corresponding to the combined thickness of the electrode with the width of the passage for the liquid, is between
20 0.2 and 9 mm, where the thickness of the electrode (13, 14) is between 0.1 and 4 mm, and the width of the passage for the liquid (19) is between 0.1 and 5 mm.
- 4) Reactor according to any of the previous claims and characterized by the fact that the depth of each electrode chamber (7, 8, 9, 10) is preferably between 1 and 5
25 mm.
- 5) Reactor according to any of the previous claims and characterized by the fact that the ratio between the width of the passage for the liquid (19) and the thickness of the electrode (13, 14) is between 0.5 and 2.
30
- 6) Reactor according to any of the previous claims and characterized by the fact that the membrane (12) is tightened between two flat, facing and opposing electrodes

(13, 14), each one in direct contact with a respective side of said membrane (12), and the membrane portion tightened between the electrodes is coplanar with the membrane edge tightened between the two bodies (5 and 6) of the reactor.

- 5 7) Reactor according to any of the previous claims and characterized by the fact that the catalytic layer that covers the electrode (13, 14) is localized on the electrode face opposed to the one in direct contact with the membrane (12).
- 8) Reactor according to any of the previous claims and characterized by the fact that
10 at least one electrode (13, 14) is coated with a suitable catalyst, consisting of one or more noble metals of the platinum family (Ir, Ru, Os, Rh, Pd, Pt), their oxides, either pure or blended with other oxides, and particularly with valve metal oxides as well as oxides of titanium and tin.
- 15 9) Reactor according to any of the previous claims and characterized by the fact that the membrane (12) is shaped in form of sheet or film, in polymeric organic material, possibly halogenated, or composite (organic/inorganic), and is provided with active groups such as carboxyl, sulfonic or amine groups.
- 20 10) Reactor according to claim 6 and characterized by the fact that the membrane has a single layer or multiple layers, and may contain reinforcing plastic gratings.
- 11) Reactor according to any of the previous claims and characterized by the fact that
25 each chamber (7, 8, 9, 10) contains one or more supporting means (18) intended for touching the electrode (13, 14) while supporting it.
- 12) Reactor according to any of the previous claims and characterized by the fact that
30 each contact means (15) is orthogonal to the plane of the respective electrode (13, 14) faces and exits the chamber (7, 8, 9, 10) through a hole (17) obtained in a body (5 or 6) of the reactor, to allow electrical connection to a connection means (20); each contact means (15) including a threaded portion that can be mated with threaded nut means for connecting to the connection means(20), the latter being

provided with connections for different contact means (15), for at least two electrodes (13, 14), as well as for the electrical wiring connection to the polarity of an electric source (22).

- 5 13) Reactor according to any of the previous claims and characterized by the fact that the inlet and outlet ducts for fluids (1, 2, 3, 4, 4a), as well as that for venting the produced gases (2a), are obtained, at least in part, in the bodies (5, 6) of the reactor.
- 10 14) Reactor according to any of the previous claims and characterized by the fact that the liquid flow is adjusted so that there is an initial, single passage within the cathode chambers (7, 9), where the incoming liquid is distributed between them, and a subsequent anodic treatment in the two anode rooms (8, 10), which are passed through in sequence.
- 15 15) Reactor according to any of the previous claims and characterized by the fact that the pH of the electrochemically activated solution produced by the reactor itself is between 6.0 and 7.5.
- 20 16) Method for the electrochemical activation of diluted brines, using a reactor according to any one of claims 1-15, characterized by the fact of using a diluted brine containing an alkali metal halide in an amount between 3 and 6 g/l.
- 25 17) Method for the electrochemical activation of diluted brines according to claim 16 and characterized by the fact of using a diluted brine containing sodium chloride or potassium chloride.



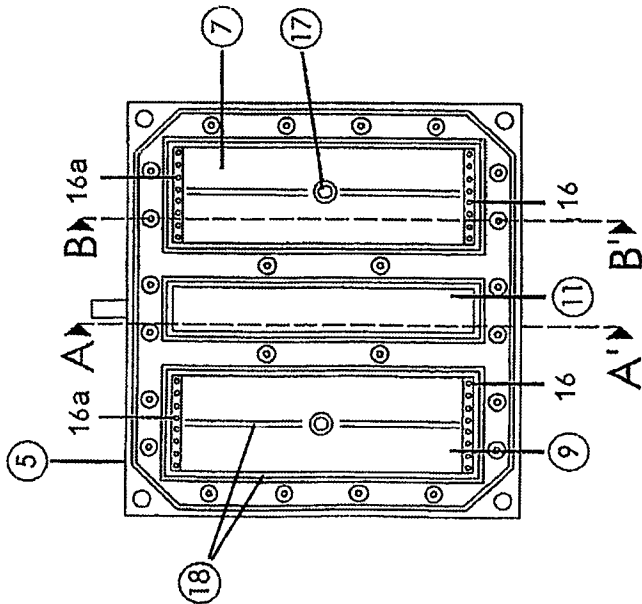


Fig. 3

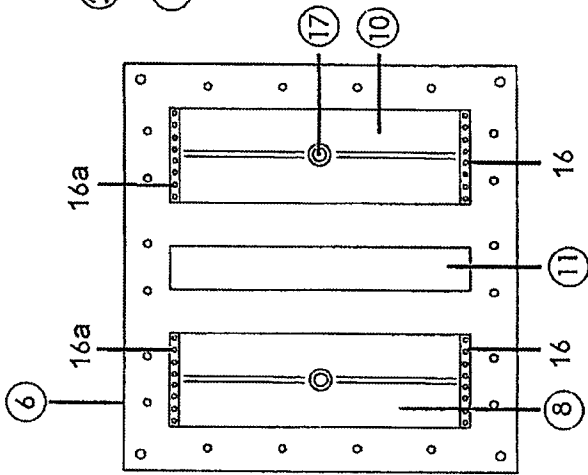


Fig. 4

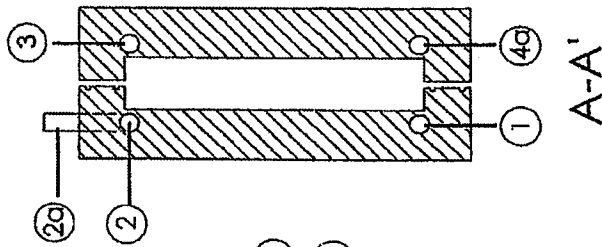
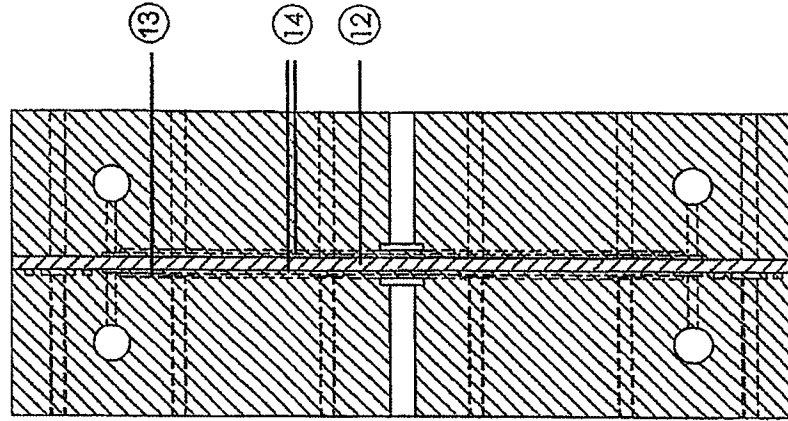


Fig. 5



B-B'

Fig. 6

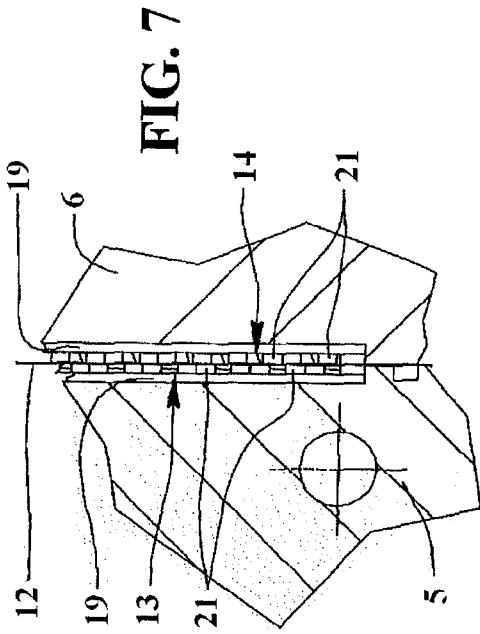


FIG. 7

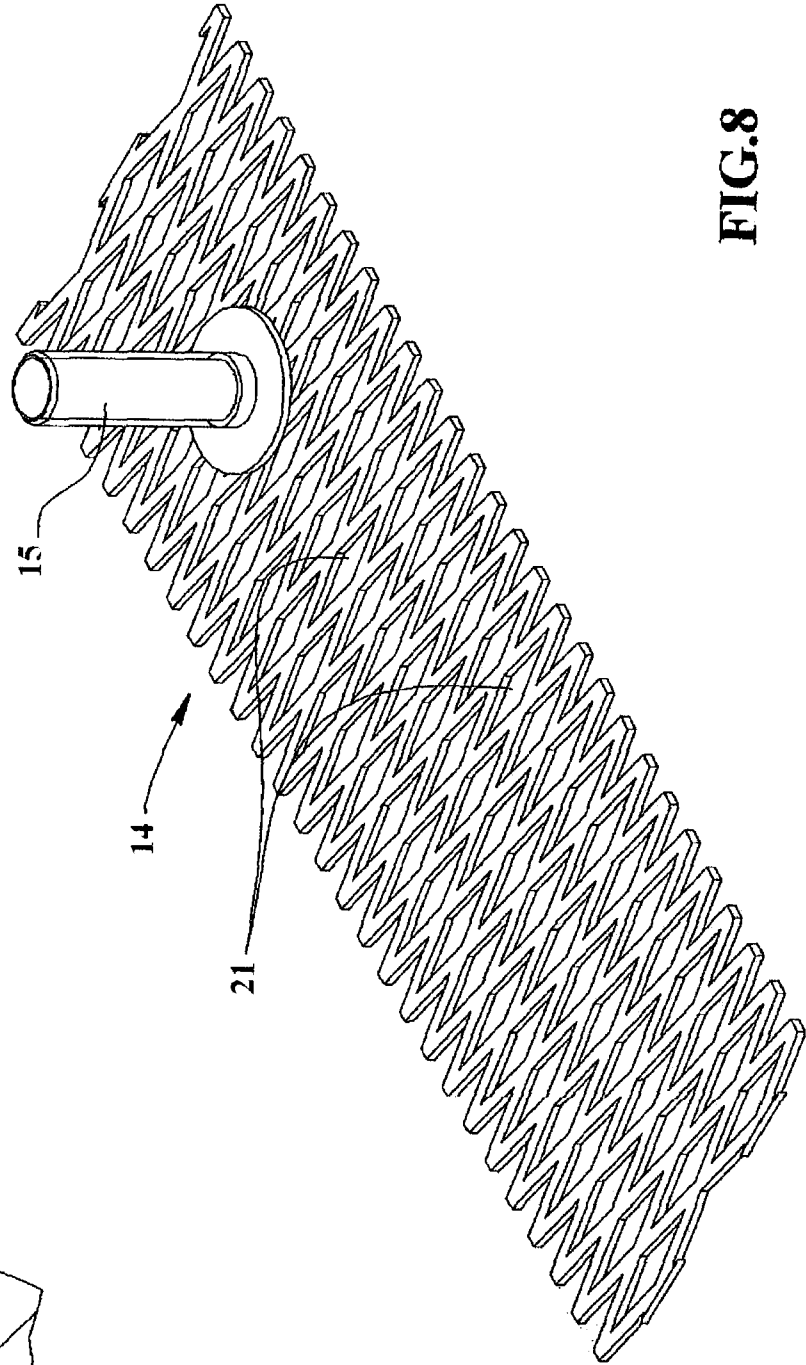


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/065077

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/461

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 741 676 A2 (PERMELEC ELECTRODE LTD [JP]; INST NAT COLLEGES TECH JAPAN [JP]) 10 January 2007 (2007-01-10) paragraph [0059] - paragraph [0065] paragraph [0071]	1-17
X	----- US 5 607 562 A (SHIMAMUNE TAKAYUKI [JP] ET AL) 4 March 1997 (1997-03-04) page 5, line 33 - page 6, line 7; figure 1; example 1	1-17
X	EP 1 754 804 A1 (TOKAI RYOKAKU TETSUDO KK [JP]) 21 February 2007 (2007-02-21) paragraph [0032] - paragraph [0045]; figures 1,2	1-17
	----- -/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

9 February 2010

18/02/2010

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Liebig, Thomas

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/065077

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 723 936 A2 (FIRST OCEAN CO LTD [JP]) 31 July 1996 (1996-07-31) page 2, line 28 - page 3, line 54; figures 1,2 -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2009/065077
--

Patent document cited in search report	Publication date	Publication date	Patent family member(s)	Publication date
EP 1741676	A2	10-01-2007	CN 1899975 A	24-01-2007
			JP 2006346203 A	28-12-2006
			KR 20060131687 A	20-12-2006
			US 2007023273 A1	01-02-2007
US 5607562	A	04-03-1997	JP 3304563 B2	22-07-2002
			JP 7109593 A	25-04-1995
EP 1754804	A1	21-02-2007	WO 2005106079 A1	10-11-2005
			JP 4220978 B2	04-02-2009
			JP 2005336607 A	08-12-2005
			US 2008053840 A1	06-03-2008
EP 0723936	A2	31-07-1996	DE 69602383 D1	17-06-1999
			DE 69602383 T2	16-09-1999
			US 5674365 A	07-10-1997