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(54) **Method and apparatus for protecting alkali chloride electrolytic cell**

(57) A method of protecting an alkali chloride electrolytic cell having a gas diffusion cathode, which comprises, on the occasion when the operation of the electrolytic cell is suspended: stopping feed of an oxygen-containing gas to a gas chamber of the cell; and substantially displacing an oxygen-containing gas atmosphere of the gas chamber with an inert gas atmosphere. Also disclosed is an apparatus for carrying out the method.

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DescriptionFIELD OF THE INVENTION

5 **[0001]** This invention relates to a method and an apparatus for protecting an alkali chloride electrolytic cell. More particularly, it relates to a method and an apparatus for protecting an alkali chloride electrolytic cell having a gas diffusion cathode, in which an alkali chloride aqueous solution is electrolyzed to produce chlorine and a caustic alkali, against performance reduction while the cell is in a suspended state.

10 RELATED ART

[0002] A method for electrolytically obtaining a caustic alkali from an alkali chloride aqueous solution by an ion-exchange membrane method which uses a gas diffusion cathode is known. This method is achieved with an electrolysis cell partitioned with an ion-exchange membrane, usually a cation-exchange membrane, into an anode chamber having
15 an anode and containing an alkali chloride aqueous solution and a cathode chamber having a gas diffusion cathode and containing water or a caustic alkali aqueous solution, and electricity is passed between the two electrodes to electrolyze the alkali chloride aqueous solution. The gas diffusion cathode is made of a porous material and supplied with an oxygen-containing gas to carry out electrolysis to obtain a caustic alkali in the cathode chamber. The merit of this technique consists in that hydrogen gas does not generate on the cathode so that the requisite electrolytic voltage is
20 markedly reduced.

[0003] Documents disclosing the above-mentioned electrolysis method includes JP-A-54-97600 (The term "JP-A" used herein means an "unexamined published Japanese patent application"), JP-A-56-44784, JP-A-56-130482, JP-A-57-152479, JP-A-59-133386, JP-A-61-266591, JP-B-58-44156 (The term "JP-B" used herein means an "examined Japanese patent publication"), JP-B-58-49639, JP-B-60-9595, and JP-B-61-20634.

25 **[0004]** While a number of proposals have hitherto been made with respect to improvement on the production method, or the performance, of a gas diffusion cathode, there are only a few on prevention of reduction in performance of a gas diffusion cathode while the operation is suspended. For example, JP-A-60-221595 teaches a method comprising diluting or displacing the electrolytic solution in the cell with water on the occasion of suspension, and JP-A-5-255882 proposes filling the cathode chamber with water or an aqueous caustic alkali saturated with hydrogen gas during
30 suspension. The present inventors have ascertained that these techniques are effective in protecting a gas diffusion cathode but, in turn, involve not a few problems.

[0005] Specifically, the method of JP-A-60-221595 which comprises dilution or displacement of the electrolytic solution in a cell with water entertains a fear of reducing the performance of the ion-exchange membrane. Where the method taught in JP-A-5-255882 which comprises filling the cathode chamber with hydrogen-saturated water or aqueous caustic alkali is followed, there is a great possibility that hydrogen gas remaining inside the gas diffusion cathode, which is permeable to gas, and the oxygen-containing gas filling the gas chamber are mixed up to form detonating gas. This system has also turned out to be problematical in the practice.

[0006] In order to operate an electrolytic cell by the ion-exchange membrane method using a gas diffusion cathode for a long period of time while maintaining the initial performance, it is important not only to set optimum conditions of
40 operation but to optimize the state of the cell during suspension of operation. A bad treatment during the suspension could result in considerable reduction of the cell performance, sometimes making the cell useless.

[0007] In the case of alkali chloride electrolysis by the ion-exchange membrane method using no gas diffusion cathode, on the other hand, the cell is partitioned with an ion-exchange membrane into an anode chamber having an anode and a cathode chamber having a cathode, and an alkali chloride aqueous solution is fed to the anode chamber, where
45 electrolysis is conducted to produce chlorine gas, while an aqueous caustic alkali or water is fed to the cathode chamber, where a caustic alkali and hydrogen gas are produced. Accordingly, during ordinary operation, the anode is noble compared with the chlorine generating potential by the chlorine overvoltage, while the cathode is less noble than the hydrogen generating potential by the hydrogen overvoltage.

[0008] On stopping the electrolytic cell, evolution of both chlorine and hydrogen also cease. In this state, the anolyte, an alkali chloride aqueous solution, has dissolved therein chlorine, and the catholyte, i.e., a caustic alkali aqueous solution has dissolved therein hydrogen. As a result, the anode and the anode chamber are kept at the chlorine generating potential, and the cathode and the cathode chamber are maintained at the hydrogen generating potential. The electrolytic cell to be used in this system is constructed of materials which can stand such voltage-potential conditions. Specifically, the anode chamber is generally made up of titanium, and the anode comprises a titanium base
50 coated with a catalyst for chlorine evolution, such as a noble metal, e.g., platinum, ruthenium, iridium, palladium or rhodium, or an oxide thereof. The cathode chamber is made of nickel or high grade stainless steel. The cathode comprises a nickel or high grade stainless steel base coated with a catalyst for hydrogen evolution.

[0009] In the alkali chloride electrolytic cell having a gas diffusion cathode, the anode is noble over the chlorine gen-

erating potential by the chlorine overvoltage as far as the cell is ordinarily operated. This is the same as in the case of the electrolysis using no gas diffusion electrode. On the other hand, the gas diffusion cathode is less noble than the oxygen reducing potential by the overvoltage. Upon stopping the cell operation, the chlorine generating reaction and the oxygen reducing reaction cease, but the potential of the anode and the anode chamber is maintained at the chlorine generating potential because the anolyte, i.e., the alkali chloride aqueous solution contains dissolved chlorine, and the gas diffusion cathode and the cathode chamber are kept at the oxygen reducing potential since the gas diffusion cathode is in contact with the caustic alkali aqueous solution and oxygen gas.

[0010] Comparing these two electrolysis systems, the anode reactions are totally the same. In other words, the anode and the anode chamber of the electrolytic cell having a gas diffusion electrode can be made of the same materials as conventionally used for those of the cell having no gas diffusion cathode. However, the cathode reactions are largely different between the two systems.

[0011] The metallic materials commonly employed to construct the cathode and the cathode chamber of a conventional ion-exchange method electrolytic cell having no gas diffusion cathode, such as nickel and stainless steel, have been regarded as being more susceptible to corrosion and having poor durability for long-term operation where used as the gas diffusion cathode or the cathode chamber.

[0012] Since silver is generally more resistant to corrosion than nickel or stainless steel and not so expensive as other noble metals, it has been attracting attention as a material that hardly corrodes and can withstand long use even under an oxidizing environment. JP-B-58-49639 proposes use of silver obtained by pyrolysis of a silver carboxylate as a catalyst. JP-A-10-158877 discloses using silver or a silver alloy for joining a conductive porous body with a gas diffusion cathode and a gas chamber. According to the teaching of JP-A-10-158878, the conductive porous body joined to the gas diffusion cathode can be made of sponge nickel coated with silver.

[0013] As long as the electrolytic cell having a gas diffusion cathode is in operation, it is true that silver is sufficiently anti-corrosive as a material making the gas diffusion cathode and the cathode chamber. Even when nickel is used, the degree of corrosion is not so notable. According to the present inventors' study, however, it has turned out that either silver or nickel has poor resistance to corrosion in the suspended state of the cell. Seeing the case where silver is used as a catalyst, it may exert a fatal influence for silver to have poor anti-corrosion. Cases are sometimes met with in which even a noble metal, such as platinum, which may be used as a catalyst of a gas diffusion cathode, is corroded at an oxygen reducing potential.

SUMMARY OF THE INVENTION

[0014] It is therefore an object of the present invention to provide a method and an apparatus for protecting an alkali chloride electrolytic cell having a gas diffusion cathode which is used to electrolyze an alkali chloride aqueous solution to produce chlorine and a caustic alkali, by which deterioration of the gas diffusion cathode and corrosion of the cathode chamber are prevented while the operation of the cell is suspended thereby to maintain the initial performance of the cell for an extended period of time.

[0015] Other objects and effects of the present invention will become apparent from the following description.

[0016] The present inventors have extensively studied on a method for producing chlorine and a caustic alkali by electrolyzing an alkali chloride aqueous solution in an electrolytic cell having a gas diffusion cathode, particularly a countermeasure against corrosion of the gas diffusion cathode and the cathode chamber while the operation of the cell is suspended. They have found as a result that the above objects of the invention can be achieved by providing the following methods and apparatus.

(1) A method of protecting an alkali chloride electrolytic cell having a gas diffusion cathode, which comprises, on the occasion when the operation of the electrolytic cell is suspended:

stopping feed of an oxygen-containing gas to a gas chamber of the cell; and substantially displacing an oxygen-containing gas atmosphere of the gas chamber with an inert gas atmosphere.

(2) The method according to the above method (1), wherein said inert gas is nitrogen.

(3) An apparatus for protecting an alkali chloride electrolytic cell having a gas diffusion cathode, which has an automatic protection system for carrying out an operation of stopping oxygen-containing gas feed to a gas chamber of the cell and an operation of displacing the atmosphere of the gas chamber with an inert gas on the occasion when the operation of the electrolytic cell is suspended.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

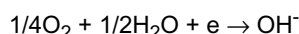
Fig. 1 is a schematic illustration of an electrolytic cell by an ion-exchange membrane method using a gas diffusion cathode, which is partitioned into three chambers.

Fig. 2 is a schematic illustration of another electrolytic cell by an ion-exchange membrane method using a gas diffusion cathode, which is partitioned into two chambers.

Fig. 3 is an instrumentation block flowsheet in suspending electrolysis according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Alkali chloride electrolysis by the ion-exchange membrane method using a gas diffusion cathode involves a cathode reaction in which oxygen and water participate as represented by formula:



[0019] An example of the electrolytic cell by the ion-exchange membrane method using a gas diffusion cathode is schematically illustrated in Fig. 1. The electrolytic cell 1 shown in Fig. 1 is partitioned with an ion-exchange membrane 2 into an anode side and a cathode side. The whole on the anode side serves as an anode chamber 3, which has an anode 4 having a large number of openings in intimate contact with the ion-exchange membrane 2, an anolyte feed opening 5 at the bottom, and an anolyte discharge opening 6 at the top. The cathode side of the ion-exchange membrane 2 is partitioned with a gas diffusion cathode 7 into a cathode chamber 8 on the ion-exchange membrane 2 side and a gas chamber 9 on the opposite side. The cathode chamber 8 has a caustic solution feed opening 10 at the bottom and a caustic solution discharge opening 11 at the top. The gas chamber 9 has a gas feed opening 12 at the upper part and a gas discharge opening 13 at the lower part.

[0020] The mechanism of the anode chamber 3 is, in principle, the same as in the electrolytic cell by the ordinary ion-exchange membrane method using no gas diffusion cathode 7. An alkali chloride aqueous solution is supplied from the anolyte feed opening 5. On contact with the gas-permeable anode 4 the alkali chloride aqueous solution is electrolyzed to form chlorine gas and alkali metal ions and reduces its concentration. The produced chlorine gas and the thus thinned aqueous solution of the alkali chloride are discharged from the anolyte discharge opening 6. The alkali metal ions generated on the anode 4 pass through the ion-exchange membrane 2 into the cathode chamber 8.

[0021] To the cathode chamber 8 is fed a caustic alkali aqueous solution or water from the caustic solution feed opening 10 and brought into contact with the gas diffusion cathode 7, while an oxygen-containing gas is fed to the gas diffusion cathode 7 from the gas chamber 9. Thus, the electrolytic reaction according to the formula shown above takes place on the surface of the gas diffusion cathode 7. The hydroxyl ions produced react with the alkali metal ions having penetrated through the ion-exchange membrane 2 to form a caustic alkali, which is discharged from the caustic solution discharge opening 11. Thus, the caustic alkali aqueous solution or water fed through the caustic solution feed opening 10 increases the alkali concentration and is then discharged from the caustic solution discharge opening 11.

[0022] An oxygen-containing gas is fed from the gas feed opening 12 to the gas chamber 9 which is adjacent to the gas diffusion cathode 7 on the side opposite to the cathode chamber 8. Part of the oxygen participates in the reaction, and the rest is discharged from the gas discharge opening 13.

[0023] Fig. 2 schematically illustrates an example of two-chamber type electrolytic cell by the ion-exchange membrane method using a gas diffusion cathode 7, in which an ion-exchange membrane 2 is provided to partition the cell into an anode chamber 3 and a cathode chamber 2. An anode 4 having a large number of openings is provided in the anode chamber 3 in intimate contact with the partitioning ion-exchange membrane 2. A gas diffusion cathode 7 is provided on the opposite side of the ion-exchange membrane 2 with a spacer (not shown) interposed therebetween. The anode chamber 3 has an anolyte feed opening 5 at the bottom and an anolyte discharge opening 6 at the top. The cathode chamber 8 has a gas/water feed opening 14 at the top and a caustic solution/exhaust gas discharge opening 15 at the bottom. The principle of the anode chamber 3 is the same as in the three chamber type cell shown in Fig. 1.

[0024] In the two-chamber type cell shown in Fig. 2, the gas diffusion cathode 7 is disposed in contact with the ion-exchange membrane 2, and the cathode chamber 8 also serves as a gas chamber. An oxygen-containing gas and water are fed to the cathode chamber 8 from the gas/water feed opening 14. Part of the water is electrolyzed in accordance with the reaction formula shown above on the surface of the gas diffusion cathode 7. The produced hydroxyl ions react with the alkali metal ions having passed through the ion-exchange membrane 2 to form a caustic alkali, which is discharged from the caustic solution/gas discharge opening 15 in the form of an aqueous solution together with the exhaust gas. The concentration of the caustic alkali aqueous solution is adjusted with water fed from the gas/water feed opening 14.

[0025] As explained above, the electrolysis by the ion-exchange membrane method using a gas diffusion electrode include a few systems. The present invention is suitably applicable to whichever system as long as an oxygen reduction reaction is conducted in a caustic alkali.

[0026] The gas diffusion cathode 7 used in the present invention can be any of various types proposed to date which comprise metal. Typical is a porous gas-permeable sheet prepared by hot pressing a mixture of carbon powder and polytetrafluoroethylene (PTFE) and having supported thereon a noble metal, such as platinum or silver or an alloy thereof, as a catalyst. The gas diffusion cathode may be combined with a metallic mesh to have increased strength or increased conductivity.

[0027] Nickel is usually used as a material forming the cathode chamber 8. Nickel coated with silver, etc. can be used to enhance anticorrosion. In the three-chamber type cell shown in Fig. 1, while no liquid flows basically in the gas chamber 9, should there be the possibility of the caustic alkali solution's leaking, considerations for anticorrosion is necessary.

[0028] While electrolysis is being performed in the above-described electrolytic cell 1, the potential of the gas diffusion cathode 7 is less noble than the oxygen reducing potential by the overvoltage. On stopping the electrolysis, the overvoltage is eliminated so that the potential is equal to the oxygen reducing potential and is noble as compared with the potential during electrolysis. If oxygen gas exists under such a condition, it is assumed that the gas diffusion cathode 7 is deteriorated and that the cathode chamber 8 is corroded.

[0029] While the electrolytic cell 1 is suspended, the feed of the oxygen-containing gas to the gas chamber 9 is stopped, but the oxygen-containing gas feed pipe and the inner wall of the gas chamber are kept exposed to the oxygen-containing gas during the suspension. Therefore, it has been found that mere stopping the oxygen-containing gas feed is insufficient for preventing the deterioration of the gas diffusion cathode and the corrosion of the cathode chamber. In order to prevent the deterioration of the gas diffusion cathode and the corrosion of the cathode chamber it is required to remove the remaining oxygen-containing gas. There are several conceivable methods that can be adopted for this purpose. The most simple and yet effective method is to displace the residual oxygen-containing gas with an inert gas. Suitable inert gases include helium, argon, and nitrogen, with nitrogen being particularly preferred for its low cost. Carbon dioxide is unfavorable because it produces an alkali carbonate in the gas diffusion cathode 7.

[0030] Since the deterioration of the gas diffusion cathode 7 and the corrosion of the cathode chamber are to be accelerated from the moment when the electrolytic cell 1 is stopped, it is necessary to carry out displacement with an inert gas immediately after the stoppage. Gas displacement is preferably conducted in an automated system.

[0031] Automatic gas displacement can preferably be effected by fitting the electrolytic cell 1 with an apparatus comprising a first sensor which detects factors for stopping the cell 1 (taken as factors A, B, C...) and emits a factor signal, an automatic stopping device which stops the operation of the cell and closes the oxygen-containing gas feed valve on receipt of the factor signal, a second sensor which confirms the closure of the oxygen-containing gas feed valve and emits a closure confirming signal, and an inert gas release device which feeds an inert gas into the gas chamber on receipt of the closure confirming signal.

[0032] The instrumentation block flowsheet of the above-described embodiment is shown in Fig. 3. The operation of the electrolytic cell 1 is stopped (block 22) on receipt of signals based on factor 21 for the stoppage. After the stoppage and on receipt of the signals teaching the stoppage of electrolysis, the oxygen feed valve of the oxygen-containing gas feed pipe is closed (block 23) and, at the same time, a nitrogen feed valve which is connected to the same pipe is opened (block 24). All these operations are automated.

[0033] The above-mentioned automatic system makes it possible to prevent the gas diffusion cathode from deterioration and the cathode chamber from corrosion while electrolysis is suspended whereby the electrolytic cell can maintain the initial performance for an extended period of time.

[0034] The present invention will now be illustrated in greater detail with reference to Examples, but it should be understood that the invention is not construed as being limited thereto.

EXAMPLE 1

[0035] Electrolysis of sodium chloride was carried out under the conditions shown below for successive 126 days. During the running test, the electrolysis was suspended after 9, 11, 12, 13, 16, 18, 23, 27, and 97 days by ceasing the oxygen gas feed and displacing with nitrogen. No abnormalities was found in the gas diffusion cathode after the 126 day electrolysis. Changes in electrolytic voltage and gas diffusion cathode overvoltage with time are shown in Table 1 below.

Condition of Electrolysis:

[0036]

- 5 Electrode area: 1 dm² (10 cm x 10 cm)
 Current density: 30 A/dm²
 Anode chamber: made of titanium
 Anode: DSE (RTM, available from Permelec Electrode Ltd.; comprising a titanium base having a coating mainly comprising RuO₂/TiO₂)
 10 Ion-exchange membrane: N954 (available from E.I. du Pont de Nemours & Co.)
 Cathode chamber: made of nickel
 Cathode: gas diffusion electrode (see below)
 Distance between electrodes: anode/ion-exchange membrane = 0 mm; ion-exchange membrane/cathode = 5 mm
 Caustic soda concentration: 32%
 15 Anolyte concentration: NaCl = 200 g/l
 Fed gas: oxygen gas of 1.6 times the theoretical

- [0037]** The gas diffusion cathode used in the cell was prepared by hot pressing into one body a gas diffusion layer made of 60 wt% of hydrophobic carbon black (acetylene black produced by Denki Kagaku Kogyo K.K.) and 40 wt% of polytetrafluoroethylene (PTFE) (D-1, available from Daikin Industries, Ltd.), a reaction layer made of 20 parts by weight of hydrophilic carbon black (AB-12, available from Denki Kagaku Kogyo K.K.) and 10 parts by weight of PTFE, and a silver mesh as a current collector, and applying thereto 3 mg/cm² of silver as a catalyst.

TABLE 1

Number of Days of Running	Electrolytic Voltage (V)	Gas Diffusion Cathode Overvoltage (V)
6	2.23	0.55
70	2.19	0.54
126	2.19	0.54

COMPARATIVE EXAMPLE 1

- [0038]** Electrolysis was carried out under the same conditions as in Example 1, except that the operation was suspended once on the 7th day for 10 hours during which oxygen was kept flowing and then resumed. The electrolytic voltage and the gas diffusion cathode overvoltage before the suspension (on the 6th day of running) were 2.18 V and 0.54 V, respectively, and those after the suspension (on the 8th day) were 2.24 V and 0.59 V, respectively. After the resumption of operation, the electrolytic voltage and the gas diffusion cathode overvoltage were 2.25 V and 0.60 V, respectively, showing no restoration. During the suspension, the circulating caustic alkali solution was found slightly green-tinged, which is assumed ascribed to nickel dissolved out of the cathode chamber.

- [0039]** The present invention provides a method and an apparatus for protecting an alkali chloride electrolytic cell having a gas diffusion cathode, by which the gas diffusion cathode is prevented from being deteriorated and the cathode chamber is prevented from being corroded while the operation of the cell is suspended thereby to maintain the initial performance of the cell for an extended period of time.

- [0040]** While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A method of protecting an alkali chloride electrolytic cell having a gas diffusion cathode, which comprises, on the occasion when the operation of the electrolytic cell is suspended:

stopping feed of an oxygen-containing gas to a gas chamber of the cell; and
 substantially displacing an oxygen-containing gas atmosphere of the gas chamber with an inert gas atmosphere.

2. The method according to claim 1, wherein said inert gas is nitrogen.

3. An apparatus for protecting an alkali chloride electrolytic cell having a gas diffusion cathode, which has an automatic protection system for carrying out an operation of stopping oxygen-containing gas feed to a gas chamber of the cell and an operation of displacing the atmosphere of the gas chamber with an inert gas on the occasion when the operation of the electrolytic cell is suspended.

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FIG. 1

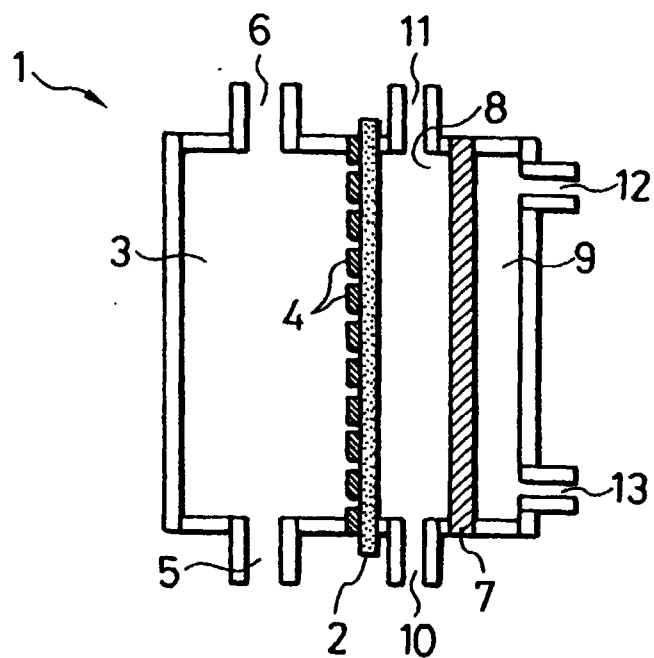


FIG. 2

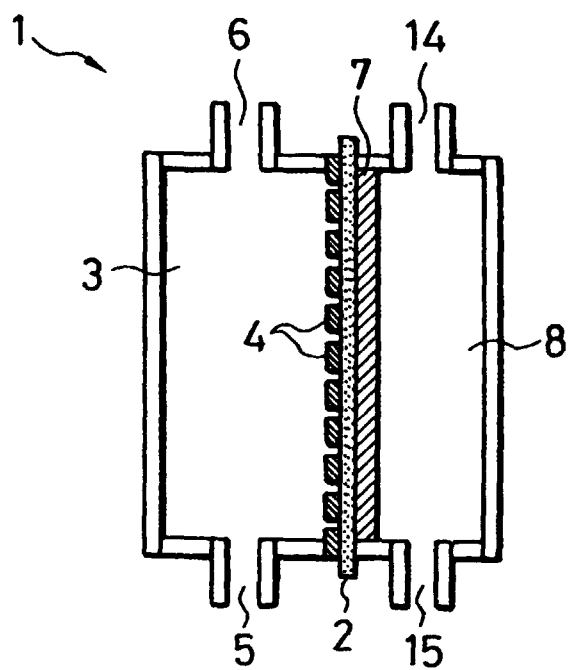
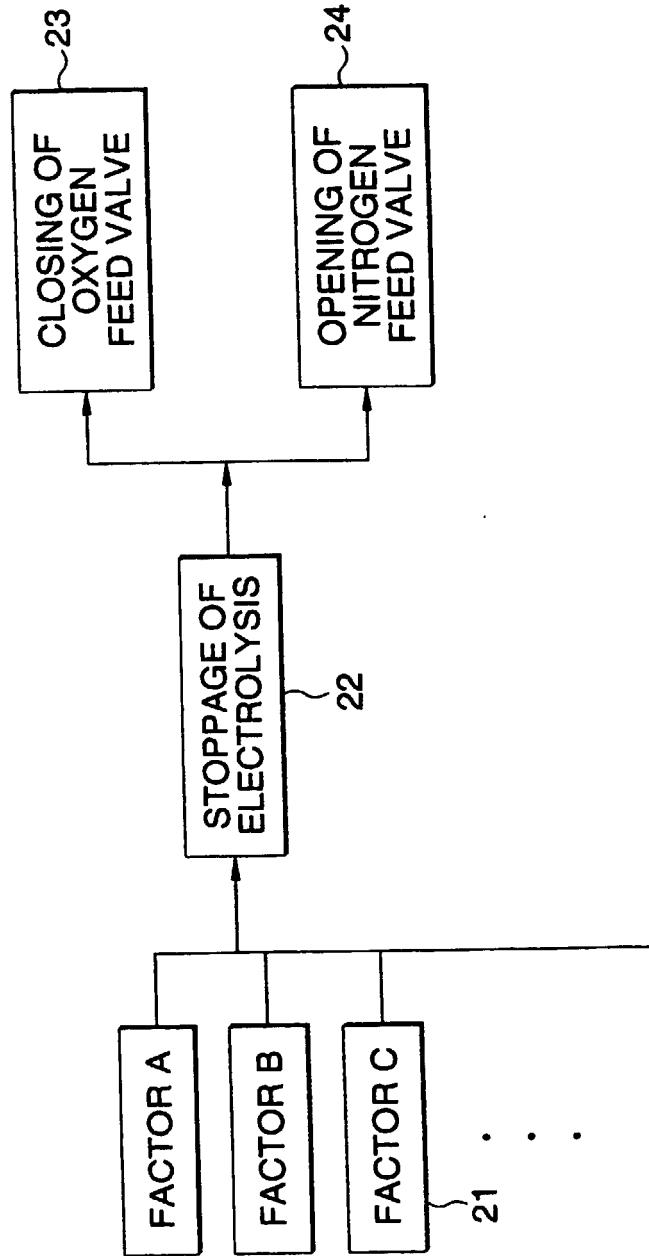


FIG. 3





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EUROPEAN SEARCH REPORT

Application Number
EP 00 11 4526

DOCUMENTS CONSIDERED TO BE RELEVANT			
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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C25B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 7 November 2000	Examiner Groseiller, P
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 00 11 4526

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