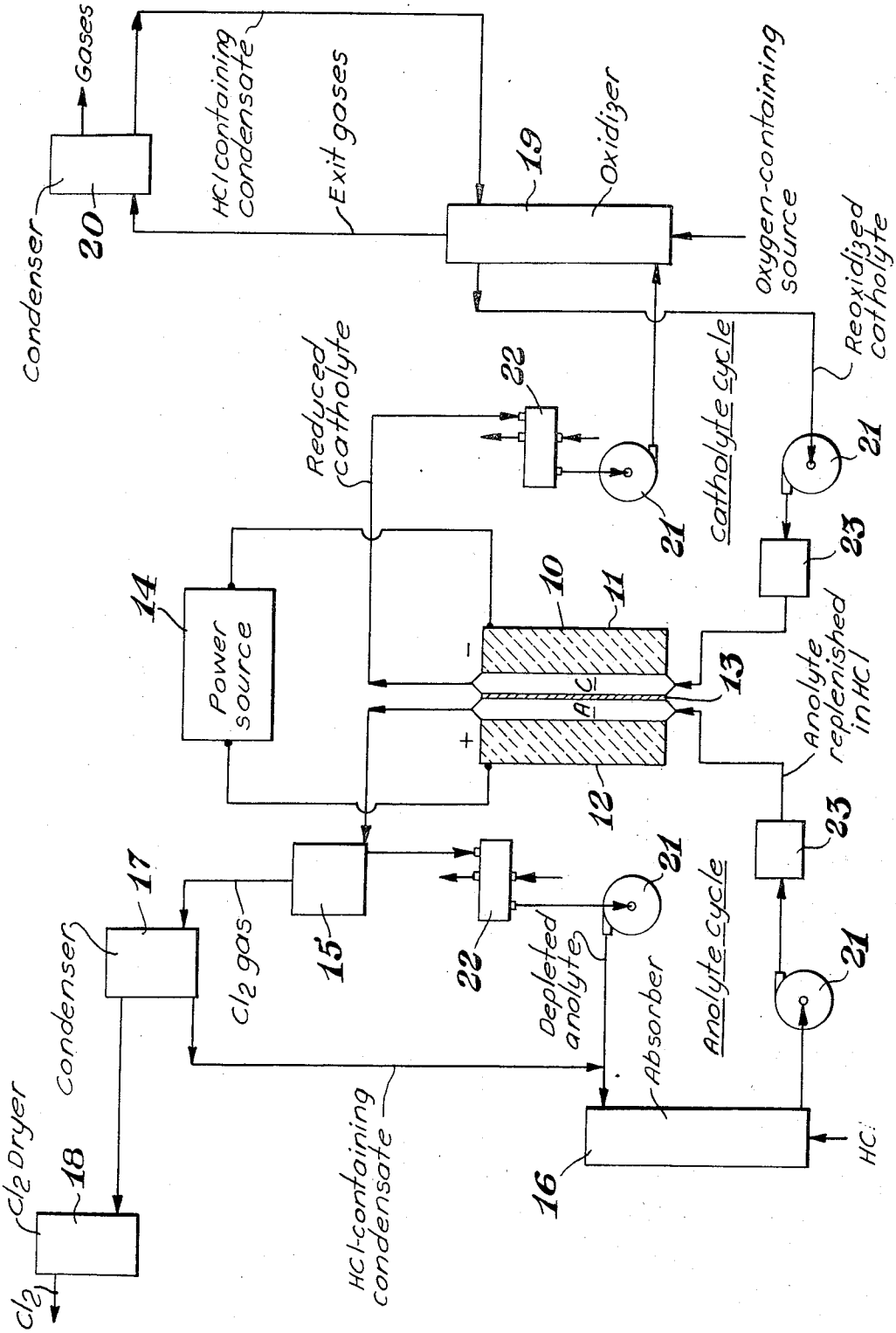
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APPARATUS FOR PREPARATION OF Cl_2 BY ELECTROLYSIS OF HCl AND POLYVALENT METAL CHLORIDE

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APPARATUS FOR PREPARATION OF Cl_2 BY ELECTROLYSIS OF HCl AND POLYVALENT METAL CHLORIDES

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U.S. Cl. 204—258 18 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to a dual electrolyte system utilizing a diaphragm electrolytic cell. The anolyte and catholyte, containing aqueous HCl and a polyvalent reducible metal chloride, are processed and recycled separately. The system of the present invention produces high purity Cl_2 at higher than conventional current efficiencies.

This is a division, of application Ser. No. 844,402, filed July 24, 1969, now U.S. 3,635,804.

BACKGROUND OF THE INVENTION

One method of producing Cl_2 by electrolysis of HCl utilizes a polyvalent metal chloride in the electrolyte solution. For example, U.S. Pat. No. 2,468,766 describes an electrolysis method which comprises: introducing an electrolyte containing HCl and a polyvalent metal chloride, e.g., $CuCl_2$, into the space between anode and cathode of a non-diaphragm cell, liberating Cl_2 at the anode, reducing the polyvalent metal chloride at the cathode, withdrawing the electrolyte through the porous cathode and reoxidizing the polyvalent metal chloride with air and HCl for recycle. Such a method does reduce the cell voltage normally necessary for direct electrolysis of HCl. However, current efficiency suffers due to the inherent flow characteristics of the system which permit back reaction of dissolved chlorine and the lower valence state metal chloride.

German Pat. 1,277,216 discloses an electrolysis system which attempts to change the electrolyte flow pattern by use of a diaphragm between the anode and cathode. By maintaining a pressure differential of zero, the diaphragm reduces reaction of the dissolved Cl_2 (anode side) with the lower valence metal chloride (cathode side). Although this does increase the current efficiency, there is still room for improvement. The German system carries out the reoxidation of the polyvalent metal chloride inside the cathode compartment of the cell. Since reoxidation is the slowest reaction taking place in the cell, this limits cell efficiency and cell size. Furthermore, improved results are only obtained using oxygen as the oxidizing gas.

It is a principal object of the present invention to provide a method and system of preparing Cl_2 by electrolysis of HCl and a polyvalent metal chloride.

A further object of the present invention is to provide such a method and system which has high current efficiency.

THE INVENTION

The above and other objects and advantages are found in the present invention which utilizes separate, dual stream flow of electrolyte containing hydrochloric acid and a reducible polyvalent metal chloride. The invention employs an electrolytic cell with a diaphragm which divides the cell into anode and cathode compartments. Anolyte and catholyte are fed into the anode and cathode

compartments. Preferably the cell is operated to achieve essentially zero fluid flow through the diaphragm.

The anolyte passes through the anode compartment where the hydrochloric acid is electrolyzed to form gaseous Cl_2. The Cl_2-containing anolyte is withdrawn from the cell and the gaseous chlorine separated from the remainder of the anolyte. The anolyte can be replenished in hydrochloric acid by absorption of HCl and recycled through the anode compartment.

The catholyte passes through the cathode compartment where polyvalent metal chloride is reduced to the lower valence state metal chloride, e.g. $CuCl_2$ reduced to Cu_2Cl_2. This reduced catholyte is removed from the cathode compartment. The metal chloride can be reoxidized to the higher valence state and the reoxidized catholyte recycled through the cathode compartment.

The dual stream method of the present invention produces high purity chlorine at extremely high current efficiency, on the order of 95%, indicating a minimum of back reaction in the cell between the chlorine produced and the lower valence state metal chloride. Further the reoxidation of the catholyte takes place outside of the cell which permits use of more versatile equipment and apparatus. This permits more efficient operation of the system since the reoxidation rate does not limit the cell reaction.

The anolyte and catholyte can contain hydrochloric acid and any polyvalent metal chloride which exists in at least two oxidation states, e.g. copper chloride, iron chloride and chromium chloride. Copper chloride is preferred. Although concentration ranges can vary quite widely and the concentrations can differ between catholyte and anolyte, a particular preferred concentration range is from about 0.5 to about 2 Molar $CuCl_2$ and from about 3 to about 8 Molar HCl. In fact, if diaphragm and process conditions are appropriate, the catholyte can be essentially polyvalent metal chloride and/or the anolyte can be essentially HCl.

The reactions taking place in the system of the present invention using an HCl-$CuCl_2$ electrolyte are as follows:

$$\text{Cathode reaction: } 2CuCl_2 \rightarrow Cu_2Cl_2 + 2Cl^-$$

$$\text{Anode reaction: } 2HCl \rightarrow 2H^+ + Cl_2$$

$$\text{Oxidation reaction: } Cu_2Cl_2 + \tfrac{1}{2}O_2 + 2H^+ + 2Cl^- \rightarrow 2CuCl_2 + H_2O$$

These reactions add up to an overall reaction of

$$2HCl + \tfrac{1}{2}O_2 \rightarrow Cl_2 + H_2O$$

PREFERRED EMBODIMENTS

The figure is a schematic flow diagram illustrating one embodiment of the dual flow electrolysis system of the present invention.

Referring to the figure, electrolytic cell **10**, composed of cathode **11**, anode **12** and diaphragm **13**, is connected to power source **14**. The materials of construction of the electrodes are those normally employed in electrolytic cells, such as carbon or graphite. Diaphragm materials can include synthetic materials which retain substantial strength and dimensional stability such as polypropylene and copolymers of vinyl chloride and acrylonitrile, and polyvinyl chloride.

The anolyte cycle comprises feeding anolyte containing hydrochloric acid and a polyvalent metal chloride is fed into the anode compartment A of the cell. The HCl in the anolyte is electrolyzed to produce Cl_2 gas. The anolyte is removed from the cell and the chlorine gas separated in a degassing unit **15**. The depleted anolyte passes through heat exchanger **22** into an absorption tower **16** where it is contacted wth HCl in gaseous or liquid form, preferably gaseous. HCl is absorbed in sufficient amount to replenish the HCl consumed during elec-

trolysis. The replenished anolyte is then recycled through a filter **23** into the cell.

The Cl_2 gas produced by the present method can be further processed by passing the gas through a condenser **17**, which removes a substantial portion of the HCl in the Cl_2 gas, and drying in chlorine dryer **18**, e.g. utilizing H_2SO_4. The HCl-containing condensate can be added back to the anolyte.

In the catholyte cycle, the catholyte is fed through the cathode compartment C where polyvalent metal chloride is reduced to the lower oxidation state. The reduced catholyte is withdrawn from the cell and carried through heat exchanger **22** to an oxidation tower where it is oxidized, for example by admixing it with an oxidizing atmosphere, e.g. oxygen-containing gas or dilute chlorine-containing gas, to reoxidize the metal chloride. While the oxidizer **19** is shown in the figure as one utilizing concurrent flow, it is understood that any tower or tank unit or the like which permits contact of the oxidizing atmosphere with the reduced anolyte is within the scope of the present system. The reoxidized anolyte is then recycled through a filter **23** into the cathode compartment.

The exit gases blown out of the oxidizing tower contain some HCl which can be recovered by passing the gases through a condenser **20**. The HCl-containing condensate can be recycled to the oxidizer. A more elaborate recovery system, which can be used but is not necessary to the present invention, is described in U.S. 2,666,024.

The anolyte and catholyte can be cycled for example by means of pumps **21** or other conventional means. It is preferable to control temperature which can be done by use of heat exchangers **22**. It is also desirable in many instances to filter the incoming electrolyte streams to remove any solids. Any type of filter means **23** can be employed.

While the figure shows a single cell system, it is understood that a series of cells connected in series could be employed in the present invention. For example, the cells could be arranged so that one side acts as the cathode for one cell and the other side acts as an anode for a second cell.

The following examples serve to further illustrate the present invention. The following general procedure and apparatus were used for the experiments. Unless otherwise indicated the term electrolyte refers to anolyte and catholyte.

A dual flow system similar to the figure was set up. Catholyte and anolyte were circulated separately by means of pumps. The flow rate could be regulated from 0 to 650 ml./min. The flow of anolyte and catholyte was measured by means of two rotameters. Copper (I) chloride formed on the cathode was reoxidized with oxygen or air in the oxidizer. The latter was made out of Pyrex glass, having an active volume of about 66 in.^{3} (21" high). The exit gas stream passed through a condenser. Oxygen or air was fed into the oxidizer through a sintered glass disc (medium size). The absorption of hydrochloric acid took place in a glass tube. The tubing for the connection was either polyethylene or pure gum rubber.

The electrode used for the cell was machined from a graphite block. The active electrode area was 15 in.^{2}, and the electrodes were spaced 1/16" from the diaphragm. All other parts except the electrode area itself were painted with Saran type cement in order to prevent electrolysis on those surfaces. Teflon or Saran type nipples were used for the inlets and outlets of the electrolyte. Two of these electrodes were clamped together with a cloth diaphragm between them to form the electrolytic cell. Leaks were minimized by a Silastic film along the 1" frame of the cell by painting the same area on the diaphragm with Saran cement and by melting the edges of the diaphragm. A copper plate to which the copper leads were soldered was bolted to the external side of each graphite plate by means of two short brass bolts. The complete setup was placed in a temperature controlled hot-box.

Hydrochloric acid concentration was determined by titration with 1 N NaOH sol. using methyl red as the indicator.

Copper (II) concentration was measured in the catholyte by the standard idometric way.

Copper (I) concentration was determined by the following procedure. A sample was quickly added to a ferric ammonium sulfate solution in sulfuric acid. The amount of iron (II) formed was oxidized to iron (III) with 0.1 N ceric sulfate solution using Ferroin as indicator.

Chlorine was absorbed in 600 ml. of a KI solution (400 g./l.) in sulfuric acid, diluted to 1000 ml., and aliquots were titrated with 0.1 N sodium thiosulfate.

Gas analyses were made with the Orsat Method.

Current efficiency is determined by comparing the actual amount of Cl_2 produced with that theoretically producible.

TABLE I

Conditions:

Composition of electrolyte: 1.505 M $CuCl_2$, 5.8 M HCl
Electrolyte flow: 610 ml./min.
Diaphram: Copolymer of vinyl chloride and acrylonitrile
Resistance between anode and cathode connectors: 33

Example No.	Current density, amps/in.^{2}	Volts	Temperature, ° C.	Current efficiency, percent
1	0.33	0.960	71	94.36
2	0.50	1.110	71	95.95
3	0.67	1.270	71	96.93
4	0.83	1.440	71	97.77
5	1.00	1.680	71	97.64
6	0.33	0.92	80	95.33
7	0.50	1.055	80	95.97
8	0.67	1.20	80	96.13
9	0.83	1.35	80	97.52
10	1.00	1.51	80	97.90

Table I shows the current efficiencies of the present system at various current densities and corresponding voltages at two temperatures. As indicated, extremely high current efficiencies, 95% or above in almost all cases, are achieved even at very low current densities, i.e. 0.33 amps/in.^{2}, and correspondingly low cell voltages, i.e. less than 1 volt.

TABLE II

Conditions:

Composition of electrolyte: 1.46 M $CuCl_2$, 5.03 M HCl
Electrolyte flow: See table below
Diaphragm: Polypropylene
Resistance: 17 milliohms
Temp.: 70–70.5° C.

Example No.	Current density, amps/in.^{2}	Volts	Electrolyte flow rate, ml./min.	Current efficiency, percent
11	0.5	0.890	610	95.97
12	0.5	0.895	510	95.97
13	0.5	0.895	400	95.97
14	0.5	0.900	300	95.32
15	0.5	0.910	215	95.75
16	1.00	1.055	610	97.69
17	1.00	1.07	510	97.69
18	1.00	1.10	400	97.69
19	1.00	1.17	300	97.47
20	0.33	0.825	510	92.75
21	0.50	0.890	510	95.32
22	0.67	0.945	510	96.13
23	0.83	0.995	510	97.13
24	1.00	1,060	510	97.68

Table II shows two aspects of the present system. First, high current efficiencies can be achieved over a wide range of electrolyte flow rates (Examples 11–15 and 16–19). These examples showed little if any decrease in current efficiency when the flow rate is decreased. Second, current efficiency can be increased by increasing the current density (Examples 20–24).

TABLE III

Conditions:

Composition of electrolyte: 1.40 M $CuCl_2$, 6.0 M HCl
Electrolyte flow: 510 ml./min.
Diaphragm: Polypropylene
Resistance: 17 milliohms
Temp.: 70–70.5° C.

Example No.	Current density, amps/in.^{2}	Volts	O_2 flow in oxidizer, ml./min.	Amount Cu^+ in reoxidized catholyte, g./l.	Current efficiency, percent
25	0.50	0.90	660	0	90.39
26	0.67	0.96	660	0	94.20
27	0.83	1.04	660	0	94.43
28	1.00	1.12	660	0	95.65
29	0.50	0.92	35	1.3	88.26
30	0.67	0.995	45	1.3	91.62
31	0.83	1.055	80	1.4	93.26
32	1.00	1.14	95	1.4	92.64
33	0.50	0.92	25	2.9	79.2
34	0.67	0.99	21	3.8	82.6
35	0.83	1.055	65	2.7	89.53
36	1.00	1.14	90	2.5	92.6

Table III reflects yet another feature of the present system—the ability to produce Cl_2 at relatively high efficiencies even with incomplete reoxidation of the polyvalent metal chloride. Examples 25–28 are similar to those shown before with a substantial excess of oxidizing gas over that sufficient to convert essentially all of the Cu_2Cl_2 to $CuCl_2$. However, even where the flow of the oxidizing gas in the oxidizer is reduced, thereby resulting in a significant amount of Cu^+ remaining in the recycled catholyte, the present system and method continue to show high current efficiencies especially at high current densities (Examples 33–36).

A representative chlorine gas analysis for any of the above examples is

	Percent
Cl_2	99.69
CO_2	0.24
O_2	0.01
N_2	0.06

Thus the system and method of the present invention can be employed to produce high purity Cl_2 from electrolysis of HCl and a polyvalent metal chloride at very high current efficiencies over wide ranges of electrolyte concentrations, current densities and flow rates.

EXAMPLES 37–41

A larger diaphragm cell, having an active electrode area of 64 sq. inches, was incorporated into the system of the present invention. The cell design was similar to that used in the previous examples. Air at a flow rate of about 42.5 liters/min. was used in the oxidation tower as the oxidizing gas.

TABLE IV

Conditions:

Composition of electrolyte: 1.46 M $CuCl_2$, 5.03 M HCl
Electrolyte flow: See table below
Diaphragm: Polypropylene
Resistance: Not measured
Temp.: 70° C.

Example no.	Current density, amps/in.^{2}	Volts	Electrolyte flow, ml./min.	Current efficiency, percent
37	0.5	0.94	85	91.4
38	0.5	0.92	185	92.0
39	0.5	0.89	400	92.0
40 [1]	0.5	1.0	760	95.5
41 [1]	0.5	1.0	190	93.2

[1] Active electrode area of 56 sq. in.; diaphragm to electrode distance of ⅛ inch.

Table IV demonstrates the high current efficiencies achieved by the present system and method using air as the oxidizing gas over a wide range of electrolyte flow rates. Examples 40 and 41 were taken from a continuously operated mini-plant setup.

EXAMPLES 42–43

If desired, the present system can be operated with different HCl concentrations in the anolyte and catholyte, with the same excellent current efficiencies, as shown by the following examples using the cell of Examples 40–41.

TABLE V

Conditions:

Composition of electrolyte: 1.50 M $CuCl_2$, 5.5 M HCl
Electrolyte flow: 180 ml./min.
Diaphragm: Polypropylene
Resistance: Not measured

Example No.	Current density, amps/in.^{2}	Volts	HCl concentrate moles/liter		Current efficiency, percent
			Anolyte	Catholyte	
42	0.5	1.02	6.0	3.8	92.1
43	0.5	1.00	7.5	4.2	91.5

What is claimed is:

1. A system for the production of chlorine by electrolysis which comprises:
   (a) at least one electrolytic cell containing an anode, a cathode, a diaphragm therebetween which separates the cell into anode and cathode compartments and connecting means to a power source;
   (b) means connected to said cell for feeding anolyte and catholyte into the anode and cathode compartments respectively of the cell, said anolyte and catholyte containing aqueous HCl and a polyvalent metal chloride; wherein Cl_2 gas is produced at the anode and polyvalent metal chloride is reduced from a higher oxidation state to a lower oxidation state at the cathode;
   (c) means connected to said cell for removing the anolyte and catholyte from the cell;
   (d) means connected to said anolyte removal means for removing the Cl_2 gas from the anolyte;
   (e) means connected to said Cl_2 removal means for absorbing additional HCl into the anolyte for recycle to the anode compartment of the cell; and
   (f) means connected to said catholyte removal means for oxidizing the reduced catholyte to reoxidize polyvalent metal chloride for recycle to the cathode compartment.

2. The system of claim 1 including a series of electrolytic cells connected in series.

3. The system of claim 1 wherein said means to reoxidize the polyvalent metal chloride is spaced apart from the cathode compartment.

4. A system for the production of chlorine by electrolysis which comprises:
   at least one electrolytic cell comprising an anode adapted to produce Cl_2 gas positioned in an anode compartment, a cathode adapted to reduce a polyvalent metal chloride from a higher oxidation state to a lower oxidation state positioned in a cathode compartment, a diaphragm adapted to separate the anode compartment from the cathode compartment, and a connecting means to a power source;
   a feed means connected to said cell and adapted to provide an anolyte to the anode compartment and a catholyte to the cathode compartment;
   an electrolyte removal means connected to said cell and adapted to remove the anolyte and the catholyte from said cell;
   a gas removal means adapted to remove the Cl_2 gas from the anolyte;
   an absorber means adapted to absorb HCl into the anolyte for recycle to the anode compartment and spaced apart from said gas removal means and the anode compartment;
   an oxidizing means adapted to reoxidize the reduced polyvalent metal chloride for recycle to the cathode

compartment connected to and spaced apart from the cathode compartment.

5. The system of claim 4 including a heat exchanger adapted to control the temperature of the anolyte.

6. The system of claim 4 including a heat exchanger adapted to control the temperature of the catholyte.

7. The system of claim 4 including filter means adapted to remove solids from the anolyte and the catholyte.

8. The system of claim 7 including two heat exchangers adapted to control the temperature of the anolyte and the catholyte, and a condenser adapted to remove HCl from exhaust gases from said oxidizing means and to recycle HCl condensate to said oxidizing means.

9. The system of claim 8 including a condenser adapted to remove HCl from the Cl_2 gas.

10. The system of claim 9 including a series of electrolytic cells connected in series.

11. The system of claim 10 wherein the anode, cathode and diaphragm are spaced apart from each other and the system is adapted to achieve a current efficiency of at least about 90 percent at a current density of up to about one ampere per square inch where the polyvalent metal chloride is completely reoxidized.

12. The system of claim 10 wherein the anode and cathode are spaced up to about 5/32 inch from the diaphragm.

13. The system of claim 4 including a condenser adapted to remove HCl from exhaust gases from said oxidizing means and to recycle HCl condensate to said oxidizing means.

14. The system of claim 4 wherein the anode and cathode are spaced up to about 5/32 inch from the diaphragm.

15. The system of claim 4 including a series of electrolytic cells connected in series.

16. The system of claim 4 wherein the anode and cathode are spaced apart from the diaphragm.

17. The system of claim 4 wherein the anode, cathode and diaphragm are spaced apart from each other and the system is adapted to achieve a current efficiency of at least about 90 percent at a current density of up to about one ampere per square inch where the polyvalent metal chloride is completely reoxidezed.

18. The system of claim 17 including a series of electrolytic cells connected in series.

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JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

U.S. Cl. X.R.

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,799,860 Dated March 26, 1974

Inventor(s) Gerhard Gritzner and James J. Leddy

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, Table I, "milliohms (70°C)" should be inserted in line 24 after "33";

Column 6, Table V, line 14, after "measured", -- Temp: 72-73°C-- should be inserted;

Column 6, line 72, after "compartment", --connected to-- should be inserted.

Signed and sealed this 3rd day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents