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Corrosion resistant electrolytic cell.

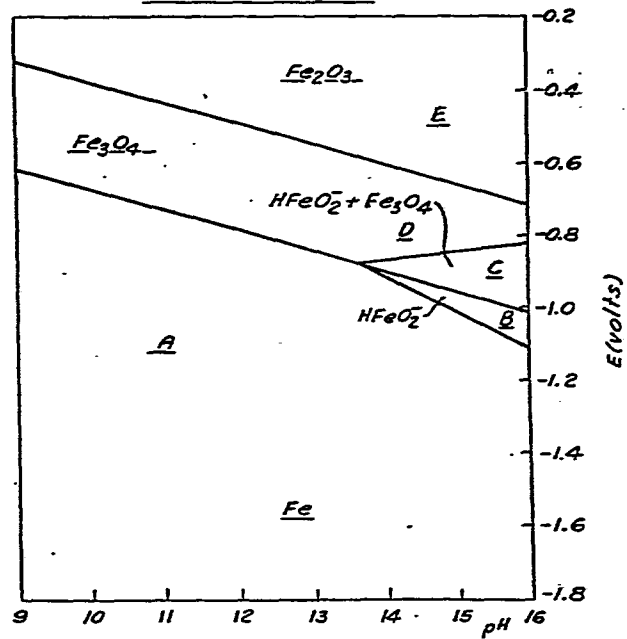
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An electrolytic cell comprising an anode, a cathode and iron-containing metals exposed to the interior portions of the cell which are maintained at about the same electrical potential as the cathode. These materials are covered with a protective coating to minimize corrosion during operation of the cell.

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POURBAIX DIAGRAM



Potential-pH equilibrium diagram for the system iron-water, at 25°C (considering as solid substances only Fe, Fe₃O₄ and Fe₂O₃)

CORROSION RESISTANT ELECTROLYTIC CELL

The present invention resides in electrolytic cells having iron-containing materials exposed to the interior portions of the cell and maintained at about the same voltage as that of the cathode.

5 Electrolytic cells have found wide uses in modern industrial practice. However, with energy costs increasing, researchers in recent years have investigated means to reduce the energy consumed by electrolytic cells, following numerous approaches. Among
10 the more common techniques used are the modification of the electrodes. For example, low overvoltage cathodes have been used; such cathodes have been described in numerous patents; among which are U.S. Patents 2,419,231; 3,272,728; 4,104,133; 4,170,536; 4,162,204; 4,024,044;
15 3,945,907 and 3,974,058.

Japanese Patent 31-6611, published August 7, 1956, discloses a nickel/zinc alloy being electroplated onto a nickel-coated, iron substrate, wherein the zinc is subsequently leached from the Ni/Zn alloy by an alkali
20 line solution. A similar process is shown in Netherlands Patent 75-07550, laid open to inspection January 20, 1976.

Accordingly, the present invention resides in an electrolytic cell wherein voltage and pH conditions place iron-containing components of the cell into a state of ionization causing deterioration of the components, said cell comprising an anode in an anode chamber; a cathode in a cathode chamber; said iron-containing components being exposed to the interior portion of the cathode chamber and electrically connected to the cathode; and wherein at least a portion of the surface of the iron-containing components is coated with a protective coating at a level sufficient to minimize ionization of iron to thereby prevent contamination of the products by electrolysis.

The Figure is a Pourbaix diagram showing the potential vs pH for an iron-water system at 25°C.

The Figure shows the oxidation state of iron as a function of pH and voltage at 25°C in an iron-water system. If the iron-containing parts of the cell exposed to pH and voltage conditions which put them into area A of the Pourbaix diagram, iron will exist as Fe. Conditions corresponding to area B, will cause iron to exist as HFeO_2^- . In area C, iron will exist as a mixture of Fe_3O_4 and HFeO_2^- . In area D, iron will exist as Fe_3O_4 while in area E, iron will exist as Fe_2O_3 . pH and voltage conditions corresponding to areas A, D and E will cause iron to exist in a solid state. However, if iron-containing parts are subjected to pH and voltage conditions corresponding to areas B or C, iron will ionize and cause iron impurities in the electrolytic products.

Although voltage reduction techniques are economical, in that they save energy, it has been

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discovered that there are problems associated with such techniques. One of the more serious problems is the fact that frequently the electrolytic products contain a greater amount of impurities than do products produced from conventional cells. For example, when low overvoltage cathodes are used in a chlor-alkali electrolytic process, it has been found that the caustic produced frequently contains a greater concentration of iron than caustic produced from cells using conventional cathodes. Since low overvoltage cathodes are typically coated with nickel or some other corrosion-resistant metal coating, it is surprising that the iron contamination in such a cell is greater than when conventional iron or steel cathodes are used.

15 It has been found that the iron contamination, present in the products produced by electrolysis when a low cathode voltage is used, comes from iron-containing cell parts which are exposed to the interior portions of the cell and are maintained at about the same voltage as the cathode. An example of a source of iron contamination is a backscreen or some other type of cathode support that is frequently used in electrolytic cells. It has been found that if at least a portion of the iron-containing metallic parts of an electrolytic cell which are exposed to the interior portions of the cell are at least partially covered with a protective coating, iron contamination in the electrolytic products is minimized.

30 The protective coating used to coat the iron-containing parts of the cell should be stable at the applied electrical voltage, substantially stable at the temperature of the cell, substantially unreactive with the catholyte, and substantially stable at the pH.

Examples of some coatings which may be used are nickel, titanium, vinyl ester resins, epoxy and various other plastics. Nickel, however, is the preferred coating since it conforms nicely to the physical and chemical requirements of the coating.

Optionally, the backscreen or other iron-containing parts of the cell may be constructed from the materials which have been listed as being good protective coatings. For example, the backscreen may be a nickel screen, rather than a nickel-coated iron screen.

When conventional iron or steel cathodes are used in an electrolytic cell for the electrolysis of water or a brine solution, the cathode is normally maintained at a voltage of approximately -1.1 to -1.2 volts vs. Normal Hydrogen Electrode (N.H.E.). The pH range is normally above approximately 13. These conditions would place iron-containing parts of the cell into area A of the Figure. Any iron present on the cathode or any other iron in the cell which is maintained at a similar voltage will not ionize but will exist as Fe. However, if the voltage is reduced so that the cathode operates at approximately -0.8 volt to approximately -1.1 volts vs. N.H.E., the cell conditions enter areas B and/or C of the Figure where HFeO_2 will form and iron will ionize. Ionization of the iron-containing parts will cause iron contamination of the products of the cell.

The invention may be used in any electrolytic cell wherein a voltage and pH conditions place iron-containing parts of the cell under conditions where

iron will ionize. In such a system, any iron-containing parts which are electrically connected with the cathode, or maintained at a voltage about the same as the cathode, will cause iron to ionize and will
9 contaminate the products of the electrolysis. The invention may be used to minimize iron contamination of the products.

It should be understood that the Pourbaix diagram which was selected for illustration of the
10 invention is for 25°C in an aqueous system which is chloride free. However, most electrolytic cells operate at elevated temperatures. For example, chlor-alkali cells normally operate at 50-100°C. The voltage
15 required to ionize iron under given pH ranges will vary with temperature, thus, while iron will ionize at voltages of about -0.8 to -1.1 volts vs. N.H.E. at 25°C, the voltage to cause ionization at 100°C in chloride-containing systems will be slightly different.

The following examples illustrate the invention
20 tion in a chlor-alkali electrolytic cell. However, it should be well understood that the invention may be used in any electrolytic cell wherein an aqueous solution is electrolyzed and wherein there are iron-containing parts electrically connected with the cathode
25 or parts which are maintained at a voltage about the same as that of the cathode.

Example

Four 11 square foot cathodes were tested in diaphragm chlor-alkali cells: One conventional low-
30 carbon steel cathode having an uncoated backscreen; one low overvoltage cathode having an uncoated backscreen;

and two low overvoltage cathodes, each having a backscreen coated with a protective nickel coating. The protective coating was applied by electroplating a steel cathode with a nickel-zinc alloy, then removing
5 the zinc by soaking in an alkaline solution, leaving a high-surface area nickel coating.

Each of the cells was fed a saturated NaCl brine solution and was maintained at a temperature of about 70°C. The same brine source fed all cells, thus
10 the brine for each cell had the same iron content. Upon start-up, each of the cells was operated at approximately 800 amps and produced an approximately 10 weight percent NaOH catholyte solution. The conventional steel cathode cell produced a catholyte having
15 1.7 ppm Fe. The low overvoltage cathode having an uncoated backscreen produced a catholyte having 1.6 ppm Fe. However, the two low overvoltage cathodes having a nickel coated backscreen produced catholytes having 0.7 and 0.5 ppm Fe, respectively.

20 After operating several weeks at 800 amps, the current on each cell was lowered to 150 amps, thus reducing the cathode overvoltage. At 150 amps, the standard steel cathode cell produced a catholyte having 0.2 ppm Fe; the low overvoltage cathode having an
25 uncoated backscreen produced a catholyte having 0.4 ppm Fe; and the two low overvoltage cathodes having nickel coated backscreens each produced catholytes having 0.06 ppm Fe.

The four cells were then shut down for a few
30 days and restarted. Upon start-up, the standard steel cathode cell produced a catholyte having 1.7 ppm Fe;

the low overvoltage cathode cell having an uncoated
backscreen produced a catholyte having 2.4 ppm Fe; and
each of the two low overvoltage cathode cells having a
coated backscreen produced catholytes having 0.5 ppm
5 Fe.

1. An electrolytic cell wherein voltage and pH conditions place iron-containing components of the cell into a state of ionization causing deterioration of the components, said cell comprising an anode in an anode chamber; a cathode in a cathode chamber; said iron-containing components being exposed to the interior portion of the cathode chamber and electrically connected to the cathode; and wherein at least a portion of the surface of the iron-containing components is coated with a protective coating at a level sufficient to minimize ionization of iron to thereby prevent contamination of the products by electrolysis.

2. The cell of Claim 1 wherein the protective coating is a metal selected from nickel or titanium or an alloy of said metals.

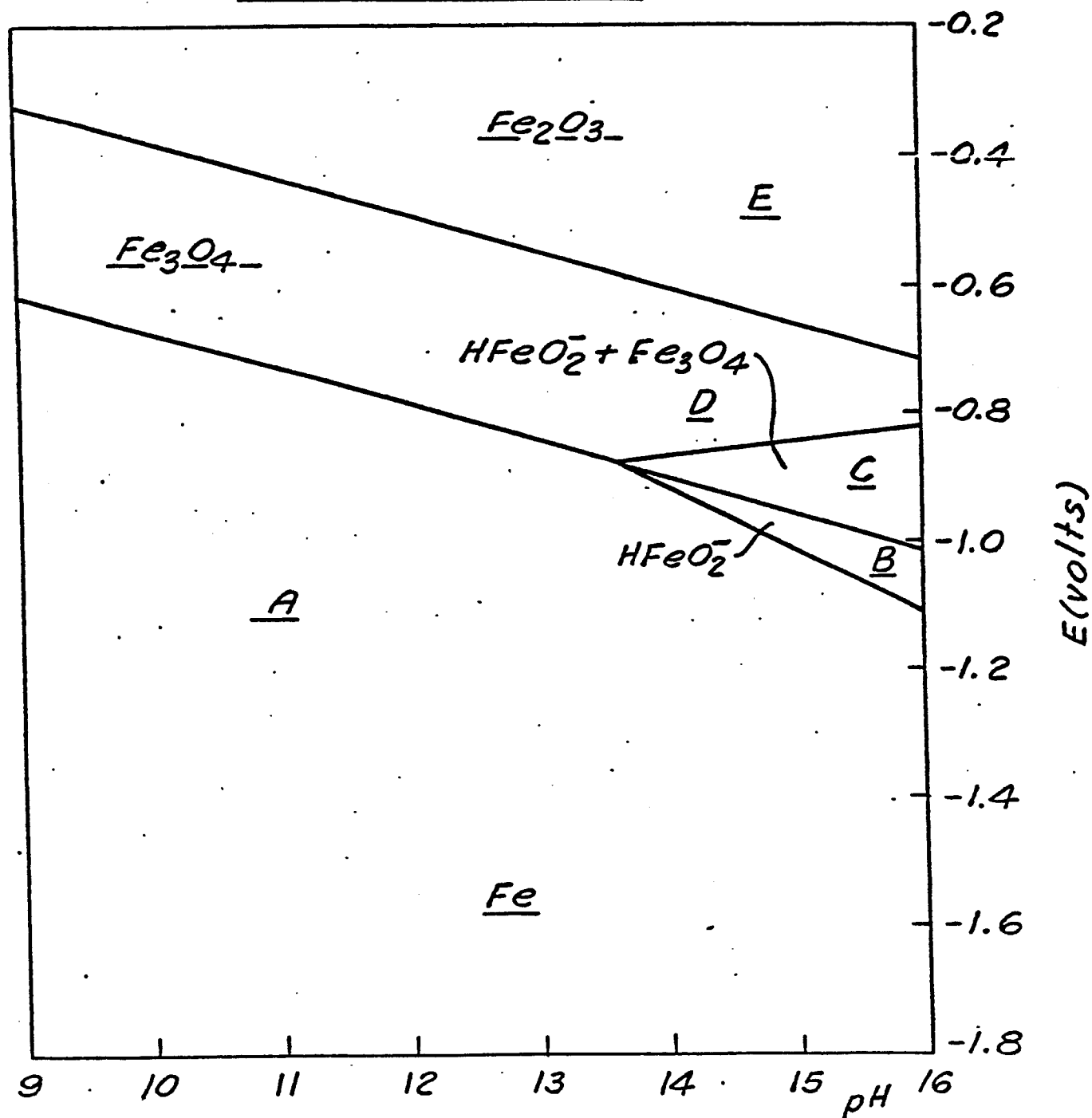
3. The cell of Claims 1 or 2, including means for impressing a sufficient voltage on the anode and the cathode to cause electrolytic reactions to occur; wherein said voltage maintains the iron containing components at a voltage level about the same as the voltage of the cathode.

4. The cell of Claim 3 wherein the cathode is maintained at a voltage of from -0.8 to -1.1 volts, vs. Normal Hydrogen Electrode.

5. The cell of Claim 3 or 4 wherein the means for maintaining the iron-containing materials at a voltage approximately the same as that of the cathode is an electrical connection between the cathode and the iron-containing materials.

6. The cell of any one of the preceding claims, wherein the cathode is a low-overflowage cathode.

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EUROPEAN SEARCH REPORT

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Application number

EP 81 10 7331

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	FR-A- 562 357 (G.F. JAUBERT) * the whole document *	1-3, 5, 6	C 25 B 9/00
A	FR-A-1 397 976 (PITTSBURGH PLATE GLASS COMPANY) * page 3, left-hand column, lines 4-37 *		
D, A	FR-A-2 278 798 (HOOKER CHEMICALS & PLASTICS CORP.)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 25 B 9/00 9/02 C 25 D 17/02
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28-05-1982	Examiner DEL PIERO G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	