United States Patent Office 3,293,161
Patented Dec. 20, 1966

3,293,161

METHOD FOR STARTING UP MERCURY CATHODE ELECTROLYTIC CELLS

Henry W. Laub, Pasadena, Tex., assignor to Oronzio de Nora Impianti Elettrochimici, Milan, Italy, a corporation of Italy

No Drawing. Filed Sept. 27, 1963, Ser. No. 311,946
7 Claims. (Cl. 204—99)

This invention relates to a method for starting up electrolytic cells having a flowing mercury cathode which is in contact with a metallic surface bearing the cathodic charge.

The invention is particularly applicable to the electrolysis for sodium chloride brine to produce chlorine and caustic soda in cells which are known in the art as horizontal mercury cells. Such cells may vary in certain construction features, but are generally similar in basic construction. A number of types are described by Sommers in "Chemical Engineering Progress," September 1957, volume 53, No. 9, pages 409 to 417.

The cells known as the horizontal type, generally consist of an elongated trough, slightly inclined towards one end, closed at the ends and top, and having a generally flat base over which mercury or mercury amalgam flows from one end of the cell to the other, forming a flowing mercury cathode. The base may be metallic such as steel, nickel clad steel, or iron; or it may be of a non-metallic material as well known in the art, with metal contacts to provide cathodic electric current.

The anodes, of graphite or suitable metal, are suspended above the flowing mercury cathode, an electrolyte solution occupies the space between the anodes and mercury, and electrolysis of the electrolyte takes place in the gap formed between the anode, and cathode surfaces.

In normal use, the base of the cell, over which the mercury cathode flows, is inclined just sufficiently to cause the mercury to flow by gravity from one end of the cell base to the other, the normal inclination from a horizontal plane passing through the high end of the cell being about 0.23° with a maximum inclination in practice of less than 0.5°. As the mercury or mercury amalgam flows from the entrance to the discharge end of the cell under electrolysis conditions, for example in the electrolysis of sodium chloride to produce chlorine and caustic soda, sodium is deposited in the flowing mercury cathode and as the mercury flows toward the discharge end of the cell more and more sodium is amalgamated therein. The mercury has a laminar flow, with sodium being amalgamated in the upper layer. In the normal operation of the horizontal mercury cell the mercury film is maintained at a minimum thickness of about .125 inch (about 3 mm.) and in order to avoid short circuits between the anode surfaces and the surface of the mercury cathode a minimum electrolyte gap of .140 inch has been found to be necessary.

In this type of cell having a metal base cathode surface, it is necessary that the mercury "wet" the metal surface completely, i.e. make contact with the actual metallic substance of the base over the entire surface area. This prevents evolution of hydrogen at the base during electrolysis and keeps the hydrogen content of the cell at a minimum.

The period of "start up" for electrolytic cells is the initial period of operation when the hydrogen content of the cell gas (chlorine) is well above the desirable one tenth of one percent for normal operation. With steel bottom cells, this period may be as much as three to four hours, during which time there are some exposed

areas of the steel not wetted by mercury which are the source of the hydrogen gas.

In my previous work with cells having a steel base and graphite anodes, I found it necessary to clean the cell bottom before the mercury would "wet" the steel. Acids were generally used to remove the oxide films, however, sometimes the use of acids would not completely remove all of the film. If there is any semblance of an oxide film or grease, or foreign matter on the cell bottom, the mercury would not "wet" the cell bottom, and would not flow properly.

Moreover, acids have other limitations which make their use undesirable. Acids also attack associated equipment, piping and the like if not made of proper materials of construction. Acids are too harsh and may pit the cathode surface. Only certain acids are effective with certain metals.

It is, therefore, an object of this invention to provide a method in mercury cathode electrolytic cells for the mercury to "wet" the cell base.

A further object is to minimize hydrogen evolution during electrolysis in mercury cathode electrolytic cells.

Another object is to provide a method for starting up mercury cathode electrolytic cells having a metallic base.

A further object is to provide a stable, reusable cleaner for mercury cathode electrolytic cells which does not attack the metal, and which may be used with all materials of construction as known in the art.

These and other objects of my invention will become apparent as the description thereof proceeds.

I have now found that the use of aqueous alkaline electrolytic cleaning solutions may be used to start up this cell for electrolysis. Such solutions have been found to be more effective than acid in preparing the cell for starting up and for obtaining a wetting of the cathodic surface with mercury.

Alkaline cleaners may be stored indefinitely and can generally be reused. These cleaners do not attack the cathode surface. Alkaline cleaners are applicable generally to all metallic materials of construction and this imposes fewer limitations with regard to materials of construction.

The use of alkaline electrolytic cleaners is known in the art of electroplating of metals. The purpose of the alkali electrolytic cleaners is to remove grease and foreign substances from the basic metal prior to the electrodeposition of the metal to be plated. The various formulations of the different alkali metal cleaners normally falls into a general pattern. The cleaners generally consist of a combination of one or more inorganic alkali metal compounds such as sodium hydroxide, sodium carbonate, sodium orthosilicate, and the like.

In starting up the cell, the method used to clean the cell base was as follows. The alkaline cleaning solution was formulated. Then the cell was filled with the cleaner. After the cell was filled, electrolysis was started with the steel bottom as a cathode, then the pumping of mercury was begun during the electrolysis. After a short period of time of mercury flow, varying from about two to ten minutes, the cathode surface was "wet" with mercury. The electric current to the cell was then shut off and the electrolytic cleaner was drained from the cell. The cell was then flushed with an electrolyte such as sodium chloride brine, then filled with brine, and normal electrolysis for the production of chlorine and caustic soda by the mercury cell process was begun.

Cleaning solutions used consisted of sodium carbonate, sodium hydroxide, and sodium orthosilicate. The proportions of the above chemicals in the cleaning solution for the operation may be varied quite widely. I have further

found that some of these materials may be eliminated from the solution. The cleaning may be accomplished without the sodium orthosilicate, and even by sodium carbonate alone.

In the Inclined Plane Mercury Cell (IPM cell), as described in copending application Serial No. 234,379, filed October 31, 1962, I found it necessary to obtain a cathode surface which was completely wet with mercury. These cells are somewhat similar in construction to the normal horizontal cells, but have an inclination from end to end of between 2° to 85° from the horizontal. In addition, the cells generally have a more permanent type of anode wherein the anode surface is titanium coated with platinum. Electrolytic cleaners essentially the same as those described above were used. The use of the cleaner in the IPM cell decreased the amount of time required to get the cell in operation considerably.

In this case, as before, it was found that the ratio of the materials in the alkaline solution is not critical and may vary over wide limits.

Because of the platinum-titanium anodes in the IPM cell, it was thought that a higher concentration of sodium carbonate would be less detrimental to the platinum anodes. The CO_2 evolved at the anodes would in all probability have less of a tendency to de-activate the anode than if oxygen were evolved, although this possibility is not definitely known. Consequently, a solution of sodium carbonate alone was used and it was found that this performed a very satisfactory job.

I have therefore determined that various formulations of the alkaline solution may be used. Table I shows the variations and the types of cells in which they are used.

TABLE I

Electrolytic cleaner composition variations

HORIZONTAL CELL—I.P.M. CELL—CARBON ANODES

	Minimum (g.p.l.)	Optimum (g.p.l.)	Maximum (g.p.l.)
Sodium Hydroxide	5	22	125
Sodium Carbonate	10	53	125
Sodium Orthosilicate	0	3	10

HORIZONTAL CELL—I.P.M. CELL—PLATINUM ANODES

Sodium Hydroxide	0	5	10
Sodium Carbonate	53	100	125
Sodium Orthosilicate	0	3	10

The compositions shown in the table represent preferred ranges and materials and are not critical limitations on the compositions. Actually the upper limit of concentration could be made to approach the limit of saturation. This is especially true of sodium carbonate.

The commercially available electrolytic cleaners generally contain a fairly high content of alkali. Alkaline salts, such as sodium carbonate, are added to control the alkalinity of the solution. The material to be cleaned is made the cathode and when current is caused to flow, a vigorous evolution of hydrogen gas occurs. The cleaning of the metal takes place fairly rapidly, partly as a result of the formation of free alkali at the cathode, and also because of the mechanical action of the hydrogen which is evolved at the metal surface. Once the cathode surface has been cleaned in this manner and the deposition of alkali metal is possible, the flowing of the mercury down the cathode produces amalgam as the direct deposition of the alkali metal takes place on the surface of the mercury. The combination of the free alkali at the cathode surface and the formation of the amalgam by the electrodeposition of the alkali metal allows the mercury to wet the surface completely and rapidly.

After the cathode surface has become amalgamated and freely wet with mercury, the interior of the cell is normally flushed with brine in order that the brine in the cell is not too alkaline when the eelctrolysis of the sodium chloride begins. The presence of a highly alkaline media during electrolysis to form chlorine results in decreased efficiency because of the production of hypochlorites.

The following specific examples are presented to illustrate the invention and to enable persons skilled in the art to better understand and practice the invention and are not intended to be limitative.

Example I

In this example, an electrolytic cell was used having a steel base and graphite electrodes. The alkaline solution consisted of water with 22 g.p.l. sodium hydroxide, 53 g.p.l. sodium carbonate, and 3 g.p.l. sodium orthosilicate.

To start up the cell, the cell was filled with the alkaline solution and the electric current was started with the steel base as the cathode. The mercury was introduced onto the base and electrolysis continued for a period of ten minutes. It was observed that the steel base was completely "wetted" with mercury at this time.

The alkaline solution was then drained from the cell, the cell was flushed with a sodium chloride brine solution for a short time and then filled with brine.

Electric current was then applied for electrolysis of the brine as conventionally done in mercury electrolysis cells. It was observed that the hydrogen gas content of the chlorine issuing from the cell was less than one-tenth of 1% (by volume) by this procedure, and this was attained in about twenty minutes or about one-eight of the time which is the usual start-up time for such cells.

In the same manner as above, an aqueous alkaline solution was used which omitted the sodium orthosilicate with comparable results.

Substantially the same results in reduction of hydrogen evolution, start-up time and improved wettability of the cathode were obtained when an aqueous sodium carbonate solution was used as recited above.

Example II

An alkaline composition similar to that of Example I, except for the omission of the sodium orthosilicate, was used with an inclined plane mercury electrolytic cell (IPM) as described above. The cell was operated at an inclination of between 2° and 85° from the horizontal. The cell had platinum coated titanium electrodes and a nickel clad steel base as the cathodic contact.

The alkaline composition was an aqueous solution containing 22 g.p.l. sodium hydroxide and 53 g.p.l. sodium carbonate.

To start up the cell, the cell was filled with the alkaline solution and the electric current was started with the steel base as the cathode. The mercury was introduced onto the base and electrolysis continued for a period of ten minutes. It was observed that the steel base was completely "wetted" with mercury at this time.

The alkaline solution was then drained from the cell, the cell was flushed with a sodium chloride brine solution for a short time and filled with brine.

Electric current was then applied for electrolysis of the brine as conventionally done in mercury electrolysis cells. It was observed that the hydrogen gas content of the chlorine issuing from the cell was less than one-tenth of 1% (by volume) by this procedure, and this was attained in about one-eighth of the time typical of the start-up time for such cells.

In the same manner as above, an aqueous alkaline solution was used which omitted the sodium orthosilicate with comparable results. Substantially the same results in reduction of hydrogen evolution, start-up time and improved wettability of the cathode were obtained when an aqueous sodium carbonate solution was used as recited above.

While I have set forth certain specific embodiments and preferred modes of practice of my invention, it will be apparent that this is only for the sake of illustration, and that various changes and modifications may be made

without departing from the spirit of the disclosure or the scope of the appended claims.

I claim:

1. A method for starting up mercury electrolytic cells having metal cathodic contact surfaces by in situ wetting of the cathodic contact surfaces with mercury amalgam, within the cell, by the use of electrolytic current which comprises: (a) introducing an aqueous alkaline solution comprising sodium carbonate into said cell in contact with said cathodic surface, (b) impressing an electrolytic current on said cell, (c) introducing mercury onto said cathodic surface, (d) continuing said electrolytic current until said cathodic surface is wetted with mercury amalgam, then stopping said current, (e) removing said alkaline solution from said cell, (f) flushing said cell with the electrolytic solution to be electrolyzed, and subsequently (g) electrolyzing said electrolytic solution in said cell.

2. A method for starting up horizontal and inclined mercury electrolytic cells having metal cathodic contact surfaces by in situ wetting of the cathodic contact surfaces with mercury amalgam, within the cell, by the use of electrolytic current which comprises: (a) introducing an aqueous alkaline solution comprising sodium carbonate into said cell in contact with said cathodic surface, (b) impressing an electrolytic current on said cell, (c) introducing mercury onto said cathodic surface, (d) continuing said electrolytic current until said cathodic surface is wetted with mercury amalgam, then stopping said current, (e) removing said alkaline solution from said cell, (f) flushing said cell with the electrolytic solution to be electrolyzed, and subsequently (g) electrolyzing said electrolytic solution in said cell.

3. A method for starting up horizontal and inclined electrolytic cells for producing chlorine and caustic soda from sodium chloride, said cells having a metal cathodic base surface by in situ wetting of the cathodic base surface with mercury amalgam which comprises: (a) introducing an aqueous alkaline solution comprising sodium carbonate into said cell in contact with said cathodic surface, (b) impressing an electrolytic current on said cell, (c) introducing mercury onto said cathodic surface, (d) continuing said electrolytic current until said cathodic surface is wetted with mercury amalgam, then stopping said current, (e) removing said alkaline solution from said cell, (f) flushing said cell with said brine solution to be electrolyzed, and subsequently (g) electrolyzing said brine solution in said cell.

4. A method for starting up mercury electrolytic cells having metal cathodic contact surfaces by in situ wetting of the cathodic contact surfaces with mercury amalgam, within the cell, by the use of electrolytic current which comprises: (a) introducing an aqueous alkaline solution of a compound selected from the group consisting of sodium hydroxide, sodium carbonate and sodium orthosilicate into said cell in contact with the cathodic surface, (b) impressing an electric current on said cell, (c) introducing mercury onto said cathodic surface, (d) continuing said electric current until said cathodic surface is wetted with mercury amalgam, then stopping said current, (e) removing said alkaline solution from said cell, (f) flushing said cell with the electrolytic solution to be electrolyzed, and subsequently (g) electrolyzing said electrolytic solution in said cell.

5. A method for starting up horizontal and inclined mercury electrolytic cells having metal cathodic contact surfaces and carbon anodes by in situ wetting of the cathodic contact surfaces with mercury amalgam within the cell by the use of electrolytic current which comprises: (a) introducing an aqueous alkaline solution comprising from about 5 to 125 g.p.l. of sodium hydroxide, from about 10 to 125 g.p.l. of sodium carbonate and from about 0 to 10 g.p.l. of sodium orthosilicate into said cell in contact with the cathodic surface, (b) impressing an electric current on said cell, (c) introducing mercury onto said cathodic surface, (d) continuing said electric current until said cathodic surface is wetted with mercury amalgam, then stopping said current, (e) removing said alkaline solution from said cell, (f) flushing said cell with the electrolytic solution to be electrolyzed, and subsequently, (g) electrolyzing said electrolytic solution in said cell.

6. A method for starting up horizontal and inclined mercury electrolytic cells having metal cathodic contact surfaces and platinum anodes by in situ wetting of the cathodic contact surfaces with mercury amalgam within the cell by the use of electrolytic current which comprises: (a) introducing an aqueous alkaline solution comprising from about 0 to 10 g.p.l. of sodium hydroxide, from about 53 to 125 g.p.l. of sodium carbonate and from about 0 to 10 g.p.l. of sodium orthosilicate into said cell in contact with the cathodic surface, (b) impressing an electric current on said cell, (c) introducing mercury onto said cathodic surface, (d) continuing said electric current until said cathodic surface is wetted with mercury amalgam, then stopping said current, (e) removing said alkaline solution from said cell, (f) flushing said cell with the electrolytic solution to be electrolyzed, and subsequently, (g) electrolyzing said electrolytic solution in said cell.

7. A method for starting up horizontal and inclined mercury electrolytic cells for producing chlorine and caustic from sodium chloride brine, said cells having metallic cathodic contact surfaces and platinum anodes by in situ wetting the cathodic contact surfaces with mercury amalgam within the cell by the use of electrolytic current which comprises: (a) introducing an aqueous alkaline solution comprising from about 0 to 10 g.p.l. of sodium hydroxide, from about 53 to 125 g.p.l. of sodium carbonate and from about 0 to 10 g.p.l. of sodium orthosilicate into said cell in contact with the cathodic surface, (b) impressing an electric current on said cell, (c) introducing mercury onto said cathodic surface, (d) continuing said electric current until said cathodic surface is wetted with mercury amalgam, then stopping said current, (e) removing said alkaline solution from said cell, (f) flushing said cell with the electrolytic solution to be electrolyzed, and subsequently, (g) electrolyzing said electrolytic solution in said cell.

References Cited by the Examiner

UNITED STATES PATENTS

3,042,602 7/1962 De Nora ---------- 204—99 X

FOREIGN PATENTS

381,049 9/1932 Great Britain.

OTHER REFERENCES

Liddiard, P. D.: Metal Industry, page 210, October 6, 1944.

Plating, pages 1267–1268, December 1950.

JOHN H. MACK, *Primary Examiner.*

H. M. FLOURNOY, *Assistant Examiner.*