May 23, 1950 E. KREBS 2,508,523

DEVICE FOR THE PROTECTION OF THE CATHODES OF ELECTROLYTIC CELLS

Filed Sept. 11, 1946

Fig.1

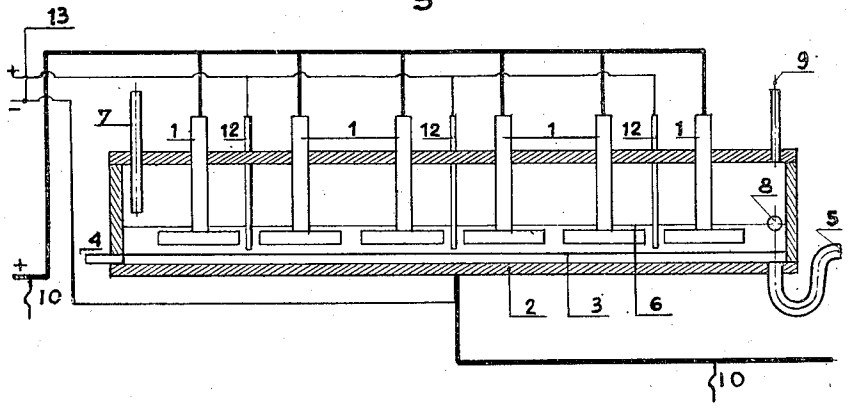


Fig.2

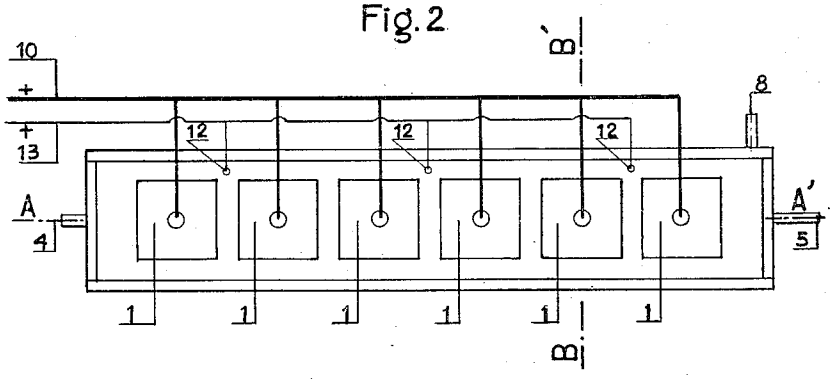
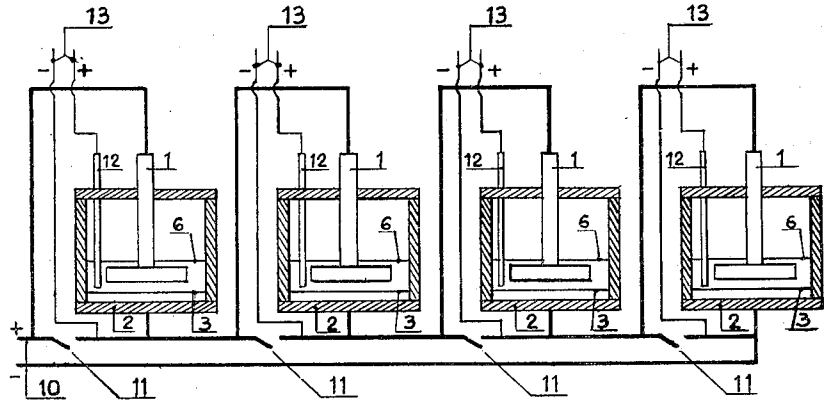


Fig.3



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Patented May 23, 1950 2,508,523

UNITED STATES PATENT OFFICE

2,508,523

DEVICE FOR THE PROTECTION OF THE CATHODES OF ELECTROLYTIC CELLS

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Application September 11, 1946, Serial No. 696,066

1 Claim. (Cl. 204—196)

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This invention relates to a device for protecting the cathodes in electrolytic cells as used for decomposing alkaline chlorides.

It is known that in some such cells, the cathode is constituted by a metal in the liquid phase, generally mercury, flowing on a fixed iron cathode, and is continuously renewed under a layer of brine constituted by a solution of the chloride which is being subjected to decomposition. Such mercury, as the electrolysis proceeds is converted into an amalgam which is at a later time decomposed in another stage.

In such installations there are generally a plurality of cells disposed in series, and it is possible if the need therefor arises (such as for cleaning, maintenance and the like) to stop the operation of any one or ones of them without thereby holding up the plant as a whole; such result is obtained by short circuiting the anodes and the cathode of one or of several cells, which has for effect to bring the anodes and the cathode to the same electric potential and breaks the flow of the electrolysis current in the desired cell or cells.

Such interruption however offers serious drawbacks, the principal ones of which are the following:

First of all, the metal forming the liquid cathode is exposed to chlorination by reason of the presence of free chlorine dissolved in the brine which coats the cathode, and if the circulation of the liquid cathode is stopped, such chlorination occurs on the fixed iron cathode as the latter is exposed by the flow of the liquid cathode. The chlorination of the liquid cathode produces a substance detrimental to the proper operation of the cell, and in the majority of cases the mercury constituting said cathode should be replaced, at the time the plant is put once more into operation, by pure mercury.

Then, chlorination of the fixed cathode entails grave defects: it gives rise, in operation of the cell, to an additional resistance to the passing of electric current and furthermore causes troublesome obstacles for the cycling of mercury and for a proper distribution or spreading thereof over the entire surface of said fixed cathode. A further detrimental result is the frequent production of local decomposition of the amalgam with resulting formation of hypochlorite and release of hydrogen which mixes with the chlorine resulting from the decomposition of the treated chloride, and the net result is the production of impure chlorine.

Moreover during said attack of the fixed cathode there is formed on the surface of the latter

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not only iron chloride but also iron oxide, both products very difficult to remove. However, in the course of the process, they do finally become gradually carried away by the liquid circulating cathode; this results in the introduction of iron amalgam into the amalgam-decomposing apparatus and the cathode product, which is generally very pure, is thereby contaminated.

In order to avoid the various above drawbacks, the brine contained in the cell is generally evacuated upon stopping; this of course entails replacing fresh brine into the cell when the latter is again connected up into the electric circuit, which constitutes a troublesome constraint. Said drawbacks may also be avoided—at least in part—by introducing into the brine in the cell, on stopping, an alkaline solution made up of the hydrate of the alkaline metal being treated, this being done in order to cause the totality of the chlorine dissolved in the brine to combine so as to reduce the tendency of the cathode to become chlorinated, but when this is done hypochlorite is formed which will later have to be eliminated from the circulating brine.

The present invention has for its object to make possible the stopping of one or more mercury cathode cells in a given installation by short circuiting said cells, the remaining cells continuing to operate and that being true without it being necessary to take any special precautions either on stopping or on restarting, all the drawbacks usually encountered being at the same time avoided.

It is known on the other hand that if during a halt, a difference of potential is maintained in the cell by any suitable means, so as to determine in said cell the flow of an electric current, the intensity of which may be very small with respect to that of the electrolysis current and insufficient to cause any substantial electrolysis effects, said current having the same direction of flow as the electrolysis current and also terminating in the cathode of the cell, the polarization of the cell being maintained, none of the above-mentioned drawbacks will occur. In order to restart it is only necessary after having started the cycling of the mercury, to re-establish the electrolysis current between the anodes and the cathode of said cell; however, inasmuch as the stopping of one or more cells has been effected by a short circuit which puts the anodes and the cathode of a given cell at the same electric potential, it will be seen that it is not possible to use, in order to cause the flow of said current which may be termed "protection current" all or

part of the anodes used for the supply of the normal electrolysis current.

The present invention contemplates, in the event where one or more cells of a given installation have been stopped, that is to say short circuited and thereby withdrawn from the effect of the electrolysis current, utilizing for supplying said cells with protection current, one or more auxiliary anodes, in suitable number and suitably located, entirely independent electrically from the anode or anodes used for supplying said cell or cells with electrolysis current; any number of cells of the installation being capable of being simultaneously subjected to the protection current and withdrawn from the action of the electrolysis current, the two latter operations being in practice carried out successively (absolute simultaneousness being of course impossible to accomplish), and being therefore separated by a certain lapse of time, which lapse is then advantageously reduced to a minimum, and the application to the cell of the protection current being preferably effected before the suppression of the electrolysis current, this being done in order to ensure the fact that at all times an electric current, whether a protection or an electrolysis current, will not fail to traverse the cell or cells in question, whereas during such stop, the remainder of the cells of the plant may continue to be supplied with electrolysis current and operate in normal conditions.

The protection current having a very low intensity, the auxiliary anodes through which said current is led in may be of relatively very small cross-section, which makes both for low cost and reduced cumbersomeness of said anodes, and the same will of course be arranged in judiciously selected numbers in various suitable locations in each cell.

It will be understood that it is then merely necessary, when a cell is short-circuited and consequently stops operating, to connect the auxiliary anodes and the cathode of said cell to any source of direct electric current under suitable tension, in order to maintain said cell polarized and avoid all the drawbacks which will result from the interruption thereof.

When the cell has been stopped and placed under the action of the protection current it may then be submitted to any desired operation and in particular cleaned.

As stated above, the electrolysis effects produced by the electrical protection supply of current are practically negligible; they only bring about an excessively low quantity of evolved chlorine. However, if it is desired completely to prevent such evolution of chlorine it will only be necessary to introduce into the cell, upon stopping, a quantity of fresh non-chlorinated brine which will take up the small amounts of chlorine thus released, by dissolving them.

In order to start operation anew, the cell which has been stopped is connected up into the circuit and the protection current supply cut off. The cell then instantaneously resumes its normal operation.

The invention makes it moreover possible simultaneously to stop one or more or even the entirety of the cells of a given installation, while maintaining the same under a protection current.

The accompanying drawings illustrate a form of embodiment of the invention; it will of course be understood that this embodiment is given merely by way of illustration and with no intention of limiting the scope of the invention, since

other devices could be constructed depending on the particular type of electrolysis elements to which it may be contemplated to apply the invention.

In the drawings, there is diagrammatically illustrated an electrolysis element or cell of the type comprising an elongated tank, wherein anodes extend throughout the entire length of the cell. The bottom of said tank, which serves the function of a fixed cathode, is slightly inclined so as to provide for the outflow of the mercury which forms the liquid cathode. Said tank is so constructed that the side walls thereof are electrically insulated with respect both to the bottom and the mercury, which both act as cathodes. In operation, the mercury, while flowing through the cell becomes loaded with the metal produced by the electrolysis reaction and flows out in the form of an amalgam which is to be decomposed elsewhere; the mercury, freed of the amalgam, is then recirculated through the cell.

The cell is sealed at its upper part by covers which should ensure a perfect seal, not only along the walls, but further at the points where the anodes extend through said covers, in such a way that the chlorine generated by electrolysis in gaseous condition may not spread out into the atmosphere of the premises wherein the cell is installed.

Figure I is an elevational view in longitudinal section on line A—A′ of Figure II of an electrolysis cell;

Figure II is a plan view of the same cell, the sealing covers being removed;

Figure III is a transverse section on B—B′ of Figure II of an installation including a plurality of electrolytic cells, illustrating the method used for connecting up said cells in series, the number of cells being limited only by the voltage selected for the direct electrolysis current.

According to the present embodiment, the electrolysis current flows from electrolysis anode **1** to the fixed cathode **2**, the mercury which forms the fluid cathode entering at **4** and leaving the cell at **5**. The brine to be decomposed is shown at **6**; it flows into the cell at **7** and out at **8**. The chlorine generated by electrolysis leaves the cell at **9**. The circuit connections for conducting the electrolysis current are shown at **10**, and the numeral **11** indicates switches which are operative when closed, to short-circuit each individual cell independently of all the others, and thus to remove it from the effect of the electrolysis current.

The auxiliary anodes such as **12**, the object of which, according to the invention, is to supply the cell with protection current, are of small sectional area and are, for instance, constituted by rods of graphite of a diameter of about 10 millimeters. They are arranged along the cell, spaced from one another by a distance which, in the present example, is about one to two meters. The number thereof in each cell is therefore small.

Inasmuch as said auxiliary anodes are located very close to the electrolysis anodes, it may be desirable to enclose them within an insulated sheath made of ebonite, for example, in order that the path of the protection current may connect with the cathode only at the base of said auxiliary anodes, and not through their sides passing through the electrolysis anodes. The protection current for each cell is supplied through lines **13**. These protection current inlets are supplied, individually for each cell, with direct current which may be derived from an auxiliary source of any suitable type, such as a storage battery, a small

auxiliary generator unit, a rectifier supplied with A. C., etc.

The above described device operates as follows: when it is desired to stop one—or several, or even the totality—of the cells in the installation, the line 13 of such cell or cells is connected to the protection current supply by any suitable means such as a switch or contact plug, then the switch 11 of each cell to be cut off is closed. The shorting of such cell or cells is thus effected without any of the cells switched out of the path of flow of the electrolysis current being at any time deprived of either protection or electrolysis current. The protection current enters each cell by way of the auxiliary anodes and leaves said cell through the fixed cathode.

In any case, neither the fixed nor the fluid cathode will be subject to the above mentioned drawbacks, the bias or polarizing voltage of the cell being at all times maintained.

When it is desired to resume operation, it is simply necessary to open the switches 11 and thereafter to cut off the supply of the auxiliary protection current or currents.

What I claim as my invention and desire to secure by Letters Patent is:

An apparatus for producing the electrolytic decomposition of an alkaline chloride comprising a plurality of electrolytic cells connected in series each including cathode means, main anode means, auxiliary anode means, a main current supply means for said apparatus, an auxiliary relatively low current supply means for said apparatus, means for connecting said cathode and said main anode means in series with each other and with said main current supply means whereby relatively high current may flow through said cells producing therein said electrolytic decomposition, means for short circuiting said cathode and said main anode means individually in each cell, and means for individually connecting said cathode and said auxiliary anode means in each cell with said auxiliary current supply means whereby relatively low current may be circulated through each of said cells producing therein substantially no electrolytic decomposition, whereby it is possible to stop operation of any of said cells severally or in combination in said apparatus while maintaining a flow of relatively low non-electrolysing current through each of said non-operating cells.

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