May 9, 1967 J. B. COTTON ETAL **3,318,792**

MERCURY CATHODE CELL WITH NOBLE METAL-TITANIUM ANODE AS COVER MEANS

Original Filed Dec. 16, 1958

3 Sheets-Sheet 1

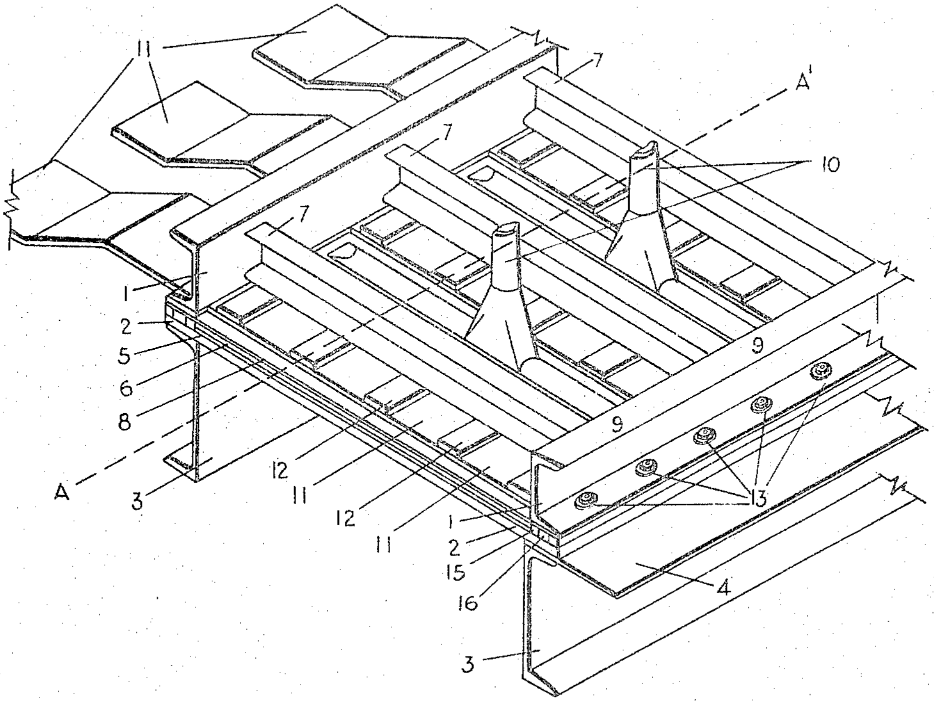

FIG 1

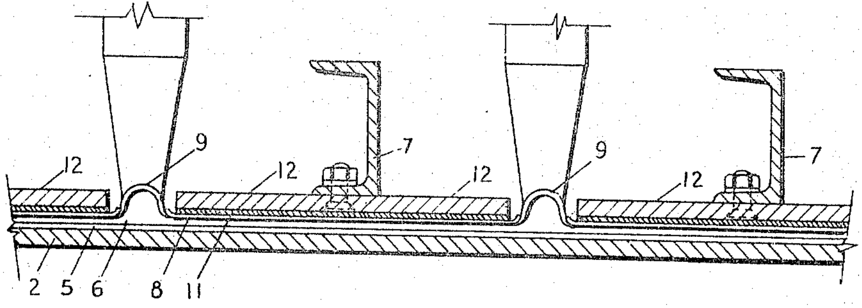

FIG. 2

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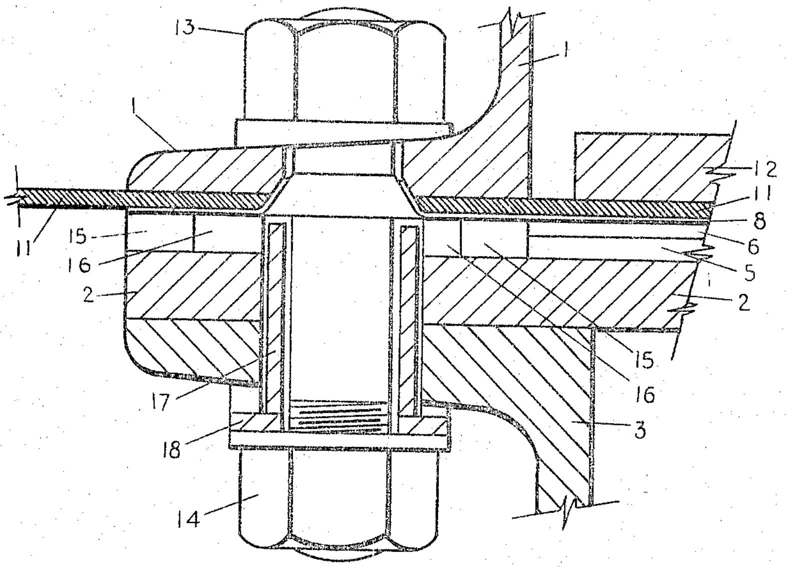

FIG. 3

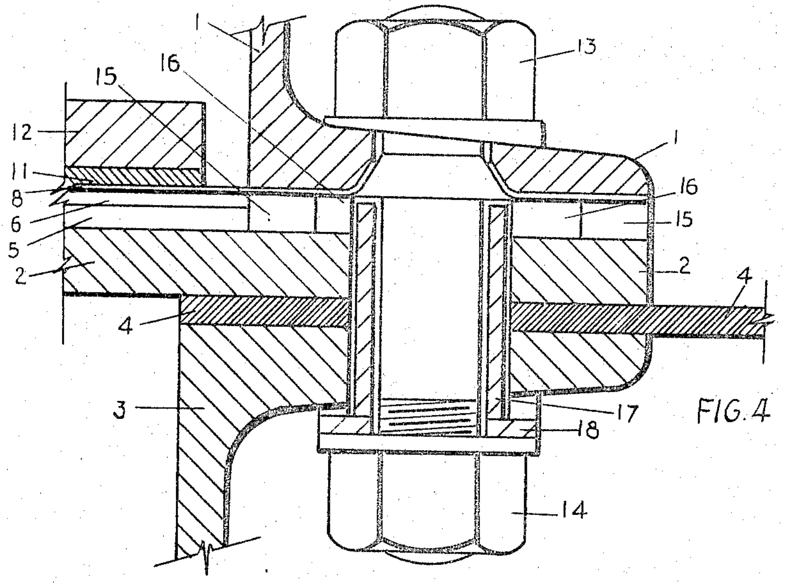

FIG. 4

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3 Sheets-Sheet 3

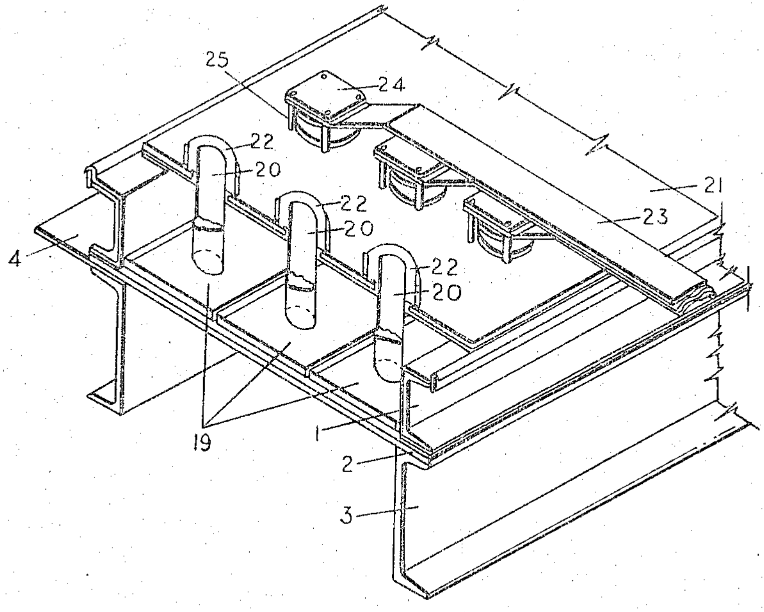

FIG. 5

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MERCURY CATHODE CELL WITH NOBLE METAL-TITANIUM ANODE AS COVER MEANS

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Continuation of application Ser. No. 780,882, Dec. 16, 1958. This application May 4, 1966, Ser. No. 548,032
Claims priority, application Great Britain, Dec. 17, 1957, 39,272/57
1 Claim. (Cl. 204—219)

This application is a continuation of Ser. No. 780,882, filled Dec. 16, 1958, now abandoned.

This invention relates to improved anodes for use in electrolytic cells for the manufacture of chlorine and caustic alkali by the electrolysis of aqueous solutions of alkali metal chlorides (hereinafter termed brine), to electrolytic cells incorporating such anodes and to the process of electrolysing brine in such cells.

Broadly, cells for the electrolysis of brine fall into two categories, namely those which employ a flowing mercury cathode and those which use a fixed cathode separated from the anode by a porous diaphragm. In the cells of the first category, the alkali metal which is the primary product discharged at the cathode forms an amalgam with the mercury which is carried away into a separate vessel, usually termed denuder, or sometimes a soda cell, where it reacts with water to form caustic alkali and hydrogen and regenerates the mercury for re-use in the primary cell. In the cells of the second category the alkali metal is discharged at a fixed cathode, usually of mild steel, and reacts at the cathode face with water from the electrolyte to form caustic alkali and liberate hydrogen. In both types of cells chlorine is discharged at the anode which is usually made of graphite. In the diagram cells a porous diaphragm is interposed between anode and cathode to prevent as far as possible mixing of the hydrogen and chlorine and mixing of the caustic alkali with the brine.

As in all electrolytic processes the potential difference that must be applied across the cell to produce continuing electrolysis can be regarded as the sum of four terms, namely the theoretical electromotive force of the cell in question, the over-voltages for the anodic product and the cathodic product at the particular surfaces used for the anode and cathode respectively, a third term representing the voltage drop along the conductors that lead the current to the anode and cathode and a fourth increment needed to overcome the ohmic resistance of the electrolyte that lies between the anode and cathode. Clearly this last term can be diminished by diminishing the distance between the electrodes and therefore, for economical running of the cell, it is necessary to maintain the electrodes as close together as is practicable.

However, in brine electrolysis the anodic product, chlorine, is decidedly corrosive and the only material that has hitherto beeen found to be practically and economically useful for constructing the anodes is graphite. Noble metals such as platinum are adequately corrosive-resistant but have been ruled out on the ground of expense. Unfortunately graphite anodes wear away with use, the surface disintegrates, carbon dioxide is formed and contaminates the chlorine and particles of carbon and impurities present in the graphite contaminate the electrolyte. Unless the graphite is selected with care some of these impurities can catalyse the formation of hydrogen at the cathode surface of a mercury cell and this hydrogen, mixing with the chlorine, can easily create a serious risk of explosion. Moreover, the wearing away of the anode progressively increases the interelectrode gap. In the simpler cells this drawback is accepted: the voltage applied to the cell is progressively increased to overcome the increasing ohmic resistance and when this becomes too great for economic operation, the cell is shut down—it may be necessary at this point to re-set the positions of the electrodes and eventually it is necessary to install a fresh anode. In more elaborately constructed cells, particularly cells with a flowing mercury cathode, provision is made so that the interelectrode gap can be adjusted progressively while the cell continues in operation, the aim being always to maintain this gap at the lowest value that is practicable. Unfortunately, however, the rate of wear of a graphite anode is seldom uniform over the whole surface and therefore even when adjustment of the anodes is provided for it is not possible to maintain the whole anode surface at the optimum distance from the cathode. For instance, in a conventional cell with a substantially horizontal flowing mercury cathode and graphite anodes in the form of blocks suspended a short distance above the mercury, the anode face wears more rapidly at the edges than in the centre and in consequence becomes rounded, so that no simple vertical adjustment of the anode can again bring all points on the anode face to an equal distance from the mercury cathode. Moreover, the various anodes is a cell frequently wear at different rates, so that to maintain optimum conditions each anode must be adjusted individually. Also the adjustment itself is a delicate matter because it is by no means easy reliably to determine, while the cell is operating, just where the electrode face is relative to the surface of the mercury cathode. To date no really satisfactory solution has been found for the various problems that arise from the wearing away of graphite anodes.

Another vexing problem in constructing and operating cells to electrolyse brine to make chlorine and caustic alkali is that of providing satisfactory internal electrical conductors or connections to the anodes. Such conductors should have low electrical resistance, should be chemically inert to hot brine containing chlorine and to moist chlorine gas, mechanically robust and resistant to internal strains set up by temperature differentials and they must also be capable of being effectively sealed into the walls or cover of the cell to form a joint impermeable to the gaseous products and to electrolyte which is apt to creep up the surface of the graphite anode and its supporting conductors. No fully satisfactory constructional material is yet available for this purpose. On the one hand, such metallic conductors as are economically practical and have appropriate electrical and mechanical properties are not adequately chemically resistant and it has not been found possible successfully to coat them with materials adequately chemically inert to the corrosive electrolyte. On the other hand graphite conductors, which are usually employed and coupled to metallic conductors outside the cell, are more difficult to fabricate to accurately defined dimensions, are apt to be fragile and to disintegrate under the internal strains set up by temperature differentials, and create difficult problems as regards sealing of the orifice through which they transverse the walls or cover of the cell. Moreover they are inherently porous and in consequence electrolyte tends to seep through the body of the conductor and escape from the cell, corroding the metallic conductors to which these graphite conductors are in turn attached. This trouble can be mitigated by impregnating the graphite with various chlorine-resistant materials, but this impregnation may in turn impair the mechanical properties of the graphite.

It has now been found that many of these difficulties are overcome if there be used, in cells for electrolysing brine for the manufacture of chlorine and caustic alkali, an anode made of a noble metal of the platinum group, namely ruthenium, rhodium, palladium, osmium, iridium or platinum (hereinafter called generically a "platinum metal") or an alloy of two or more such metals and an electrically conducting lead to such anode made of titanium or an alloy consisting essentially of titanium. It has long been known that platinum would form a chemically and mechanically stable anode for a chlorine cell but platinum (or other metal of this group) in massive form has been ruled out on the ground of expense. Also it was known that the over-voltage of chlorine on platinum is appreciably higher than on graphite. Further, there has not been available hitherto an appropriately robust and chemically inert constructional material that could serve as a mechanical support for, and provide the electrical connection to, a very thin sheet or a surface coating of a platinum metal. It has now been found that titanium or an alloy consisting essentially of titanium provides such an appropriate constructional material and that the combination of a surface of a platinum metal to provide the actual anode with a titanium or titanium alloy structure to provide the requisite mechanical support for and electrically conducting lead to the anode solves most of the problems that at present beset the design and construction of anodes for electrolytic cells for the manufacture of caustic alkali and chlorine by electrolysis of brine.

As compared with the present conventional graphite anode and graphite conducting leads the combination of an anode surface of a platinum metal with a titanium supporting and conducting lead shows the following advantages. Both the anode and the conductor are mechanically much more robust and can be fabricated much more readily and accurately to closely prescribed dimensions. Both are chemically more resistance to the corrosive action of the hot chlorine-containing brine. The platinum metal is, of course, intrinsically more resistant and the titanium becomes protected by the formation of an adherent chemically resistant surface layer. This layer also acts as an electrical insulator so that although the titanium is electrically conducting its surface is insulated and it does not itself function as an anode. Moreover this insulating layer is self-healing—that is, if it should be mechanically damaged during the installation of the anode or during the operation of the cell, the resulting local electrolytic action regenerates the protective layer and the damage is made good. The titanium conductor does not disintegrate and does not generate carbon dioxide to contaminate the chlorine, nor does it form or liberate impurities in the brine that are liable to catalyse the formation of hydrogen at the cathode of a mercury cell. The titanium is very much less liable than graphite to distort or fracture under internal strains set up by temperature differentials. It is also impervious to the electrolyte which therefore cannot seep through the material of the anode conductor to the outside of the cell. Moreover, because the titanium is more robust and more readily fabricated to accurately predetermined dimensions the cell can be more easily sealed. For instance a sheet of titanium can be made to function simultaneously as cell cover and anode support, thus eliminating any need for anode conductors to pass through orifices in the walls or cover of the cell. Finally, and perhaps most important, the anode and its support can be fashioned with much greater precision than a graphite anode and once it has been placed in proper relationship to the cathode, no problems of periodic adjustment arise because the new anode wears away very much more slowly and such wear as does occur does not sensibly increase the interelectrode gap. The requisite close setting, once achieved, is thereafter maintained indefinitely. In consequence the ohmic resistance of the electrolyte lying between anode and cathode, and therefore, the potential difference needed to overcome this resistance, can be brought to the minimum practicable value and will then remain at that value with a consequent considerable saving of electrical energy; the cell will indeed consistently operate at the optimum energy consumption.

Naturally, since the operative anode surface is of a platinum metal, an all-important feature of the design of such a cell is the provision of means whereby the thinnest possible layer of the platinum metal can be accurately supported at the appropriate very short distance from the cathode and fed with an adequate supply of electrical energy. One therefore arrives at the concept of a block or plate of titanium or titanium alloy serving as support and electrically conducting lead for a film or surface coating of a platinum metal secured or deposited thereon in any convenient manner, this film or coating of the platinum metal being the operative anode. Further, since titanium itself is still relatively expensive and has an appreciably lower electrical conductivity than, say, copper or aluminium, one can utilise a support and electrical lead constructed of a cheaper and/or more electrically conductive metal, for instance copper, aluminium or even steel, clad first with titanium and then having the operative anode face which will be opposed to the cathode covered with a layer of the platinum metal. Such a structure can, if desired, be made with a series of ports or channels communicating with orifices scattered over the face of the anode so as to allow the chlorine which is there liberated to escape more rapidly from the anode surface and pass away through the off-take pipe which is located in the upper part of the cell. Indeed one can visualise, for example, an exceedingly simple form of cell with a substantially horizontal cathode, for instance a flowing mercury cathode, utilising high speed brine flow and consisting of a trough-shaped base plate to bear the mercury cathode, insulating sides and a single block or plate of titanium or titanium-clad steel serving at once as the cell cover, electrically conducting lead and anode support, the lower face thereof being covered or coated with a platinum metal to provide the operative anode and the plate or block being pierced at appropriate intervals to provide off-take ports through which the chlorine is removed from the cell.

The facing or coating of a platinum metal which provides the real anode surface may be consistuted, if desired, by a thin sheet or foil which is welded to the titanium support. However, it is preferred to use a layer of the platinum metal electrolytically deposited on the titanium surface, since in this way a given weight of the platinum metal can be spread over a greater surface of titanium. Also it has been found that the over-voltage of chlorine on an electrolytically prepared platinum surface appears to be less than on a surface of massive platinum such as a sheet or foil; indeed it is comparable with the over-voltage on graphite. If desired, other methods may likewise be utilised for applying the requisite coating of a platinum metal to the titanium support, for example, roll-bonding, cathode sputtering, vacuum deposition, metal spraying, rolling a platinum metal powder into the surface of a titanium sheet and painting of a titanium structure with a conventional metallising solution and subsequently heating in the manner practised in the ceramics industry.

In the foregoing discussion the invention has been more particularly described and illustrated with reference to a brine cell having a substantially horizontal flowing mercury cathode but, as has already been indicated and as will be readily apparent to those skilled in this art, the new combination of a platinum metal anode and a titanium supporting lead is equally applicable to a cell with a substantially vertical flowing mercury cathode and likewise to a diaphragm cell. Such cells also customarily incorporate graphite anodes and hence suffer most of the disadvantages and occasion most of the difficulties discussed above; consequently their economy, smoothness of operation and ease of fabrication and maintenance are likewise very considerably improved by the incorporation therein of the new combination of an anode surface of a platinum metal and a supporting and conducting lead of titanium or an alloy consisting essentially of titanium.

One convenient way of embodying this invention in a design for a high speed brine cell having a substantially horizontal flowing mercury cathode is illustrated in FIGURES 1, 2, 3 and 4 of the accompanying drawings wherein FIGURE 1 represents, in isometric projection, a view of a transverse section of the cell, FIGURE 2 represents a longitudinal section along the line A–A^1, and FIGURES 3 and 4 are sectional details of the edges of the cell showing how the various constructional members are assembled together.

In each of the figures (which are not drawn to scale), the side members **1** and base plate **2**, together with appropriate end members (not shown) define a long rectangular box-like cell borne on channel-shaped supporting members **3**, all these being conveniently made of mild steel. A copper cathode lead **4** is clamped between the supporting member **3** and the base plate **2** and thus provides an electrical connection to the mercury cathode **5** which flows along the cell on the surface of the base plate **2**. Above the mercury cathode **5** is the space occupied by the electrolyte **6**. Above the electrolyte space **6**, the anode assembly is supported by the transverse steel anode frames **7** which in turn are carried on the side members **1**. The essential portion of the anode structure is a continuous titanium sheet **8** the underface of which is covered with an electrolytically deposited coating of platinum; this sheet is clamped at the edges between the side members **1** and ebonite spacers **15** lying on the base plate **2**, so that it serves simultaneously as the anode and as a cover for the cell. This sheet has at intervals transverse corrugations **9** which serve as channels wherein the chlorine liberated at the anode face collects and which lead to chlorine off-takes **10**. Bonded to the upper face of the titanium anode sheet **8** and covering the whole of its upper face between one corrugation and the next are a series of copper strips **11** which carry the current to the anode. As will be seen from the drawings, the portions of the copper strips which are positioned on the upper face of the titanium sheet are coterminous with the platinised area on the underface of the sheet. In the embodiment illustrated, the strips also extend beyond the titanium sheet as shown in FIGURE 1 for the indicated current connection. As already indicated, this composite anode assembly is carried on the transverse anode frames **7**. However, as will be appreciated, the brine must be fed to a cell of this kind under considerable pressure and the copper-bonded titanium sheet which forms the actual cell cover is not of itself rigid enough to resist deformation under that brine pressure. Therefore a series of steel reinforcing strips **12**, running longitudinally along the cell are inserted between the anode sheet **8** and the transverse anode frames **7** and secured to the latter by means of clips or in any other convenient manner.

Referring now more particularly to FIGURES 3 and 4, these show, in greater detail, how the edges of the cell are sealed and the various constructional members assembled together. As depicted in FIGURE 3, which shows the anode edge of the cell, the base plate **2** rests on the supporting member **3**; above this are the ebonite spacing strip **15** and rubber packing **16** and above these again are the platinised titanium anode **8** and its copper lead **11**. All these members are clamped between the side frame **1** and the supporting member **3** by means of the bolts and nuts **13** and **14** respectively. The base plate **2**, the ebonite spacer **15** and the platinised face of the titanium anode sheet **8** define the actual cell space within which are contained the mercury **5** and the brine **6**. Since the bolt **13** makes contact with the anode sheet **8** (via the side member **1** and the copper anode lead **11**) and the supporting member **3** makes contact with the mercury cathode **5** (via the base plate **2**), an insulating sleeve **17** and an insulating washer **18** are inserted to prevent bolt **13** from making contact with base plate **2** or supporting member **3**. In FIGURE 4, which depicts the cathode edge of the cell, the arrangement is a little different since the copper lead **4** in this case makes contact with the base plate **2**. Other parts (similarly numbered in all the figures) serve the same purposes as already described in connection with FIGURE 3.

FIGURE 5 illustrates how the invention may be utilised in a more orthodox design of mercury cell utilising a lower rate of brine flow; it depicts, in isometric projection, a transverse section across the cell. As in FIGURES 1–4, the steel base plate **2**, which bears the mercury cathode **5**, is clamped between the side members **1** and the supporting members **3**. The copper cathode lead **4** is held between the base plate **2** and the supporting member **3**. Titanium anode plates **19**, platinised on the underface, are supported on titanium rods **20** which hold them below the brine surface and at the requisite distance from the mercury cathode **5**. The rods **20** pass through the cell cover **21** and are surrounded at their upper extremities by collars **22** which seal the orifice through which the rods traverse the cover. Copper anode leads **23** are clamped to the upper faces of the titanium rods **20** and collars **22** by means of the plates **24** and bolts **25**. In cells of this design the brine is not fed under high pressure and does not fill all the cell space; the chlorine accumulates in the upper part of the cell and is taken off by a pipe (not shown) at the end of the cell.

As will be apparent from the foregoing, the present process for preparing chlorine and caustic alkali may be described as comprising the steps of providing an aqueous solution of an alkali metal chloride in an electrolytic cell, the cell having as the anode an operative surface of a metal selected from the group consisting of platinum, rhodium, alloys which are largely rhodium and alloys which are largely platinum, and electrical conducting means within the cell operatively associated with the surface to lead current to said surface, the conducting means consisting essentially of titanium and thereafter supplying an electrolyzing current to the anode through the conducting means. Use of the anodes described herein for cathodic protection is disclosed and claimed in the commonly assigned Cotton et al. application Ser. No. 748,938, filed July 16, 1958.

What we claim is:

A cell for electrolyzing an aqueous solution of an alkali metal chloride, said cell comprising a substantially horizontal flowing mercury cathode and, positioned above and substantially parallel therewith, an anode which is a surface coating of a metal selected from the group consisting of platinum, rhodium, alloys which are largely platinum and alloys which are largely rhodium, carried on the underface of a sheet which consists essentially of titanium, said sheet constituting and functioning simultaneously as the cell cover, the anode support and the electrically conducting means which leads electrolyzing current to the anode, said cell also including a layer of metal more conductive than titanium in contact with the upper face of said sheet and extending thereover so as to be at least coterminous with said surface coating.

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