United States Patent [19]

Koziol et al.

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[45] **Oct. 1, 1974**

[54] **ELECTROLYSIS CELL**

[75] Inventors: **Konrad Koziol,** Rothenbach; **Karl-Heinz Sieberer,** Zirndorf; **Baptist Zenk; Hans-Carl Rathjen,** both of Rothenbach, all of Germany

[73] Assignee: **C. Conradty,** Nurnberg, Germany

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[52] **U.S. Cl.**.............. **204/219,** 204/284, 204/290 F

[51] **Int. Cl.**............................ **C22d 1/04,** B01k 3/04

[58] **Field of Search**............................ 204/219–220, 204/250, 284, 290 F

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Primary Examiner—John H. Mack
Assistant Examiner—D. R. Valentine
Attorney, Agent, or Firm—Walter Becker

[57] **ABSTRACT**

An electrolysis cell, particularly an amalgam cell, in which beams of conductive metal, such as copper or aluminum, are mounted above the cell and have contact strips secured to the bottom which are resistant to chemical attach with shielding means connected to the contact strips and isolating the beams from the interior of the cell. Suspended from the contact strips are anode elements in the form of bars or a grid or grate of metal resistant to chemical attack. The anode members can also be suspended from the beams by studs of metal resistant to chemical attack and to which the shield referred to is connected so that in every case the beams are isolated from the inside of the cell and thus are not subject to attack by chlorine gas.

19 Claims, 30 Drawing Figures

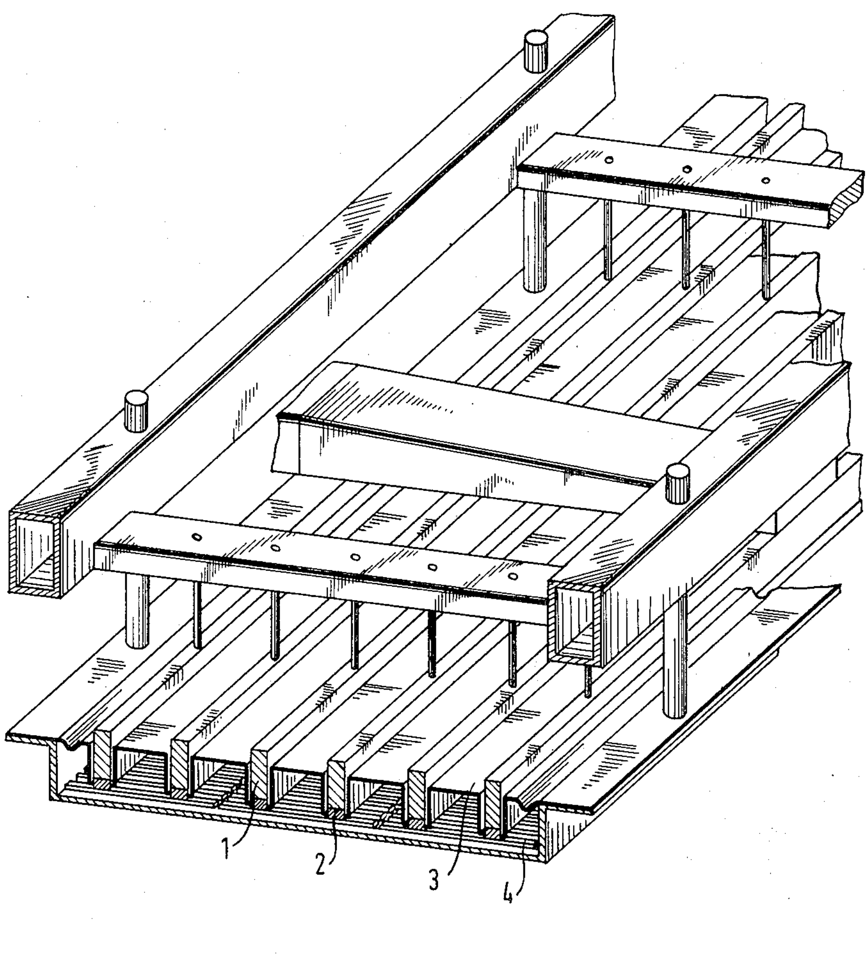


Fig. 1

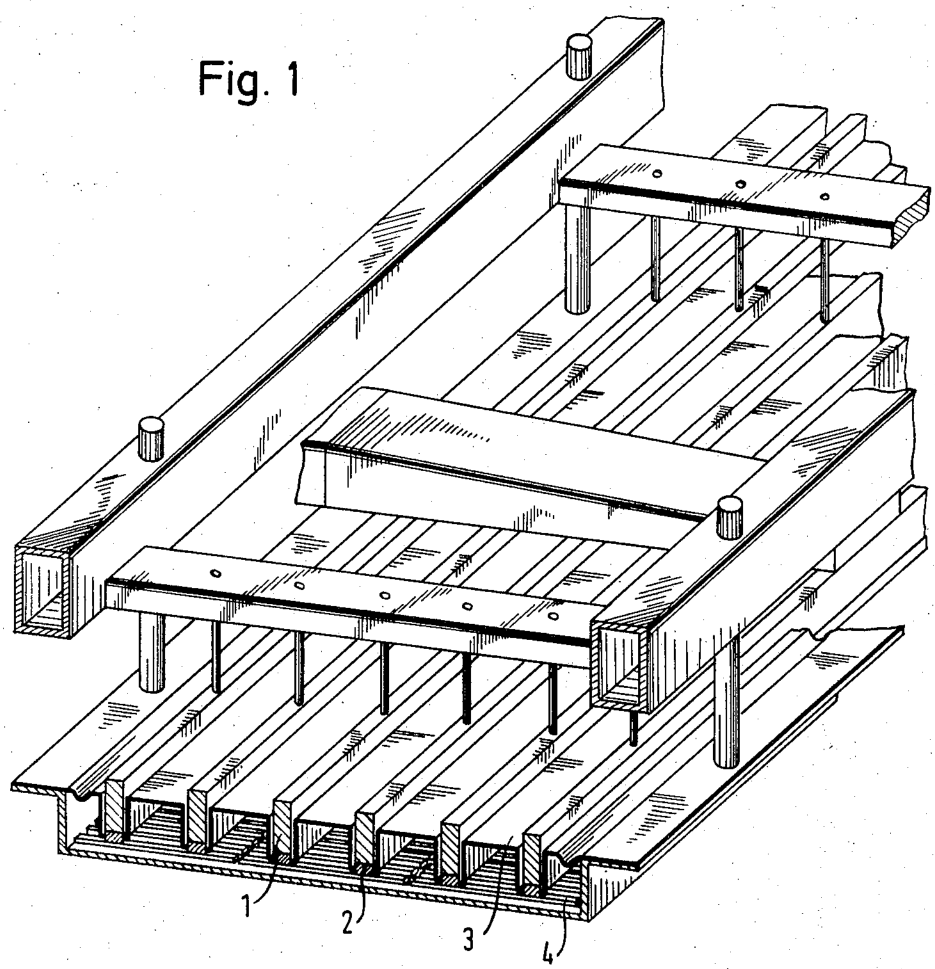


Fig. 2

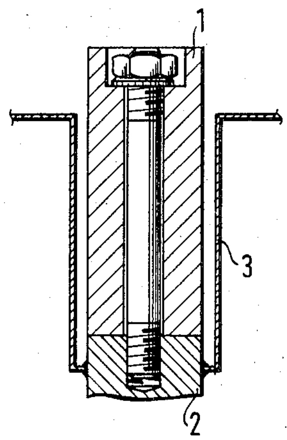


Fig. 3

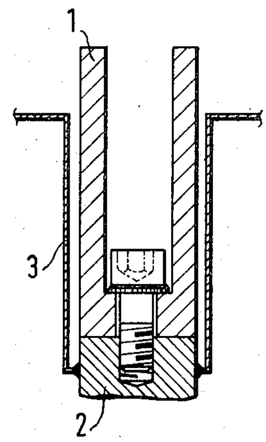


Fig. 4

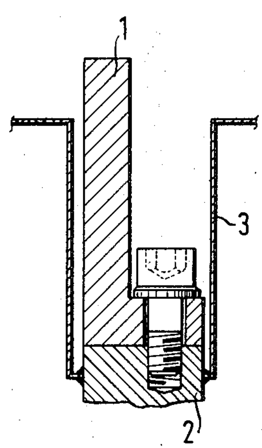
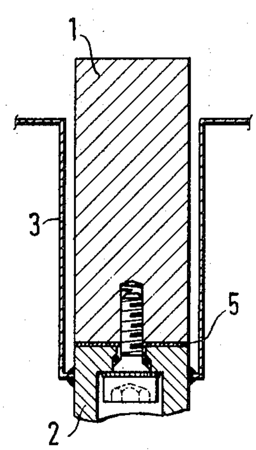


Fig. 5



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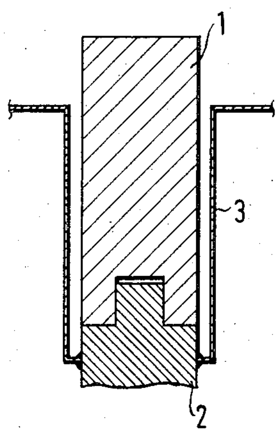


Fig. 7

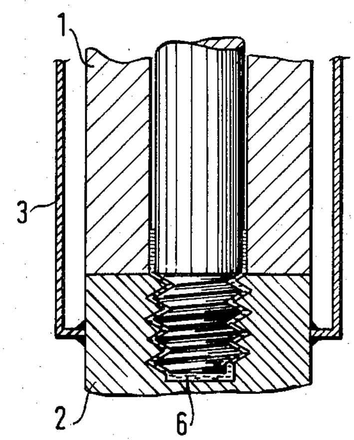


Fig. 8

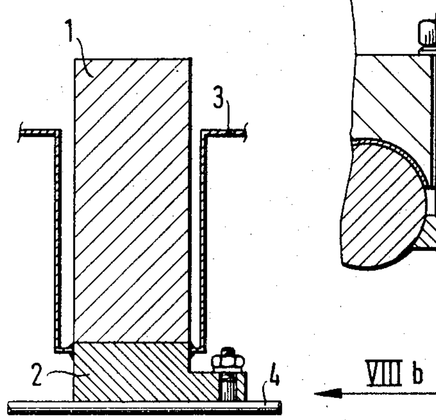


Fig. 8a

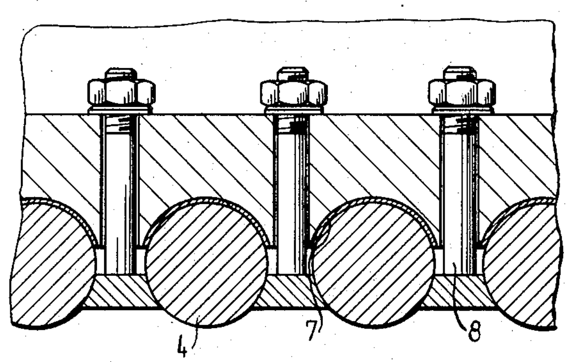


Fig. 8 b

Fig. 9

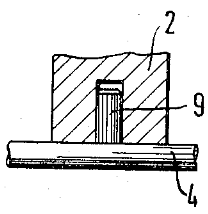
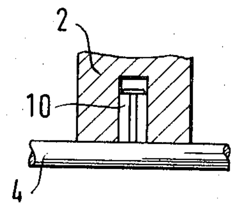


Fig. 10



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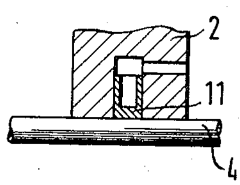

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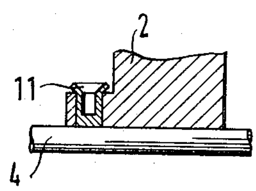


Fig. 13

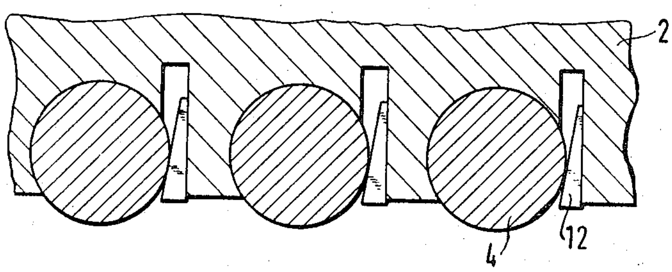
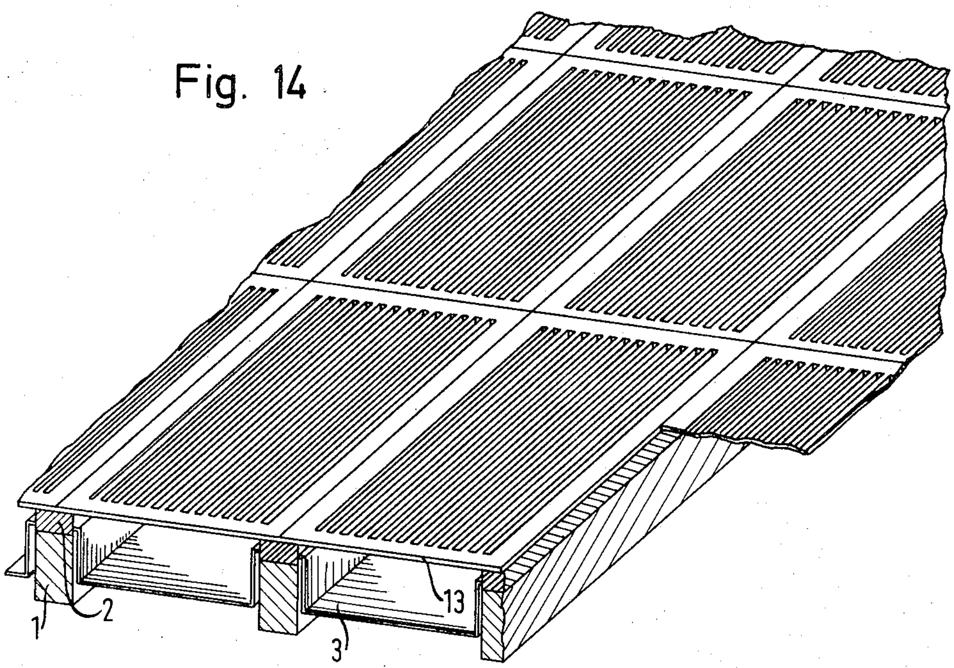


Fig. 14



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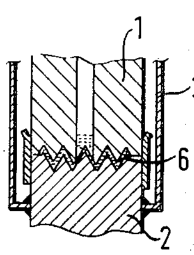
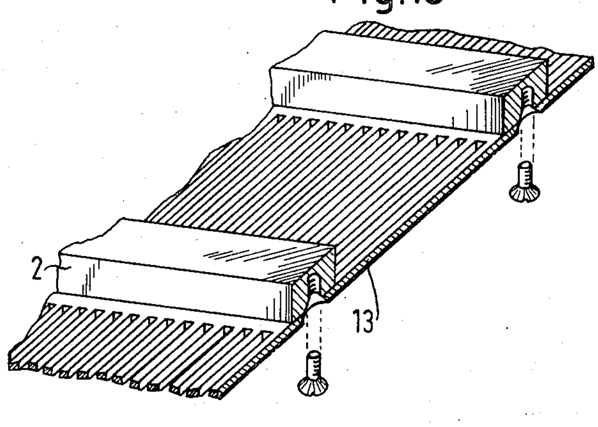


Fig.16



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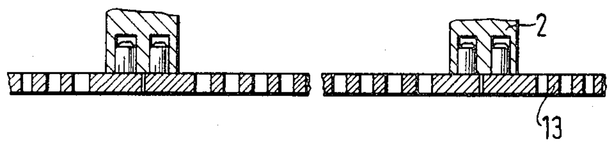

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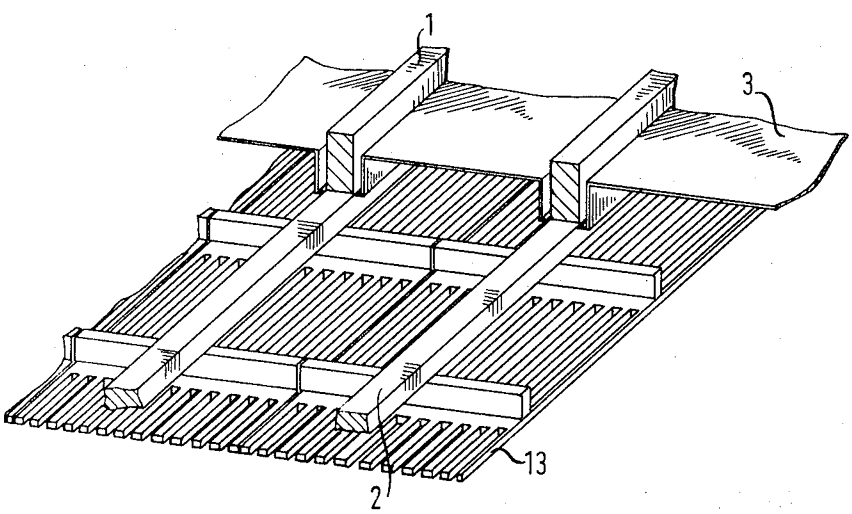

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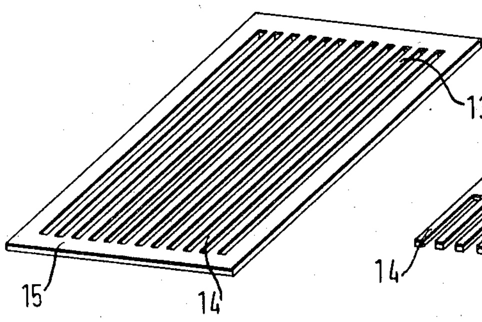

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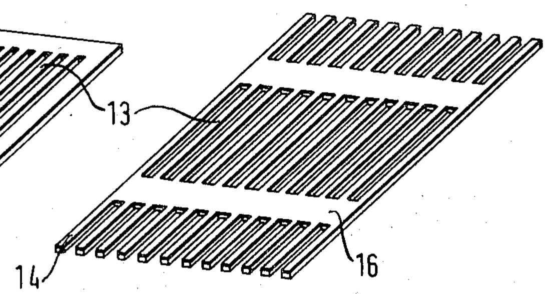

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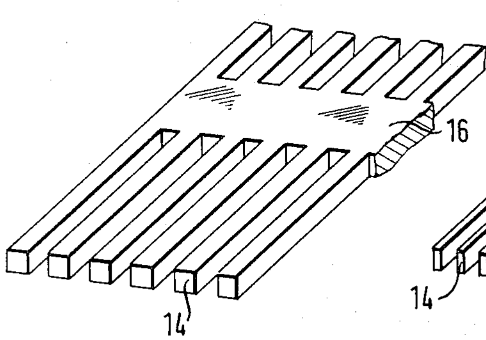

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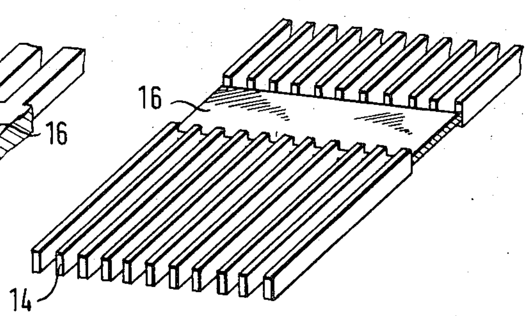

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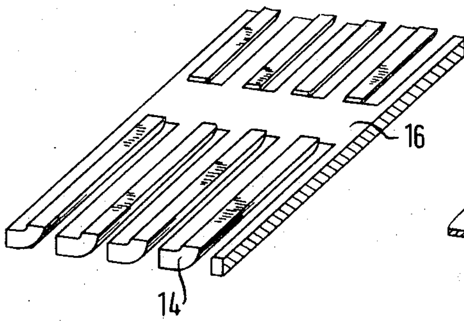

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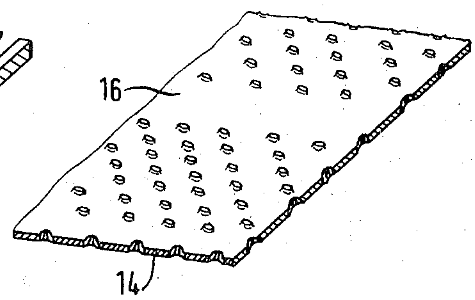
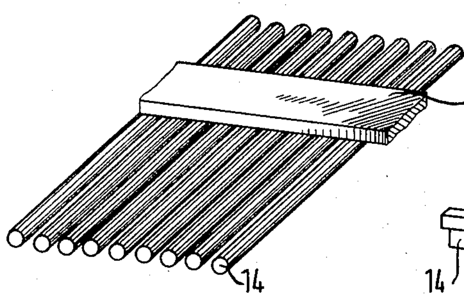


Fig. 25



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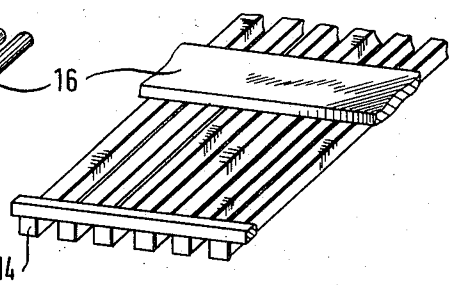


Fig. 27

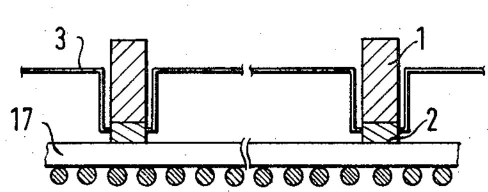


Fig. 28

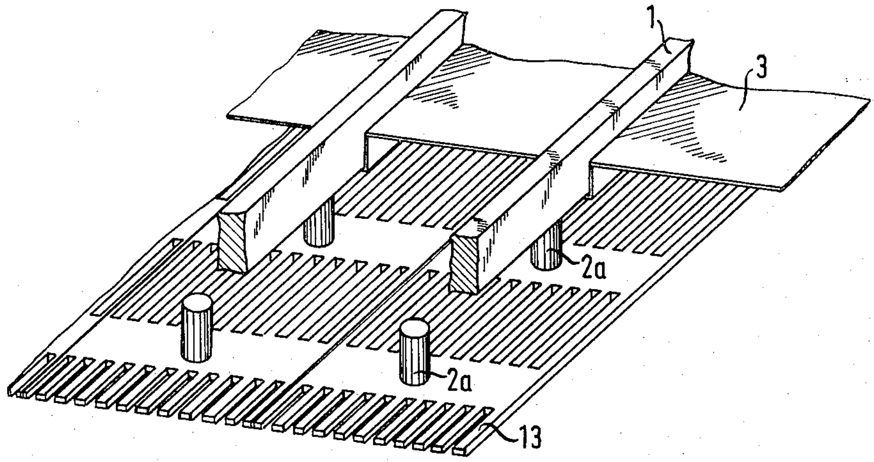
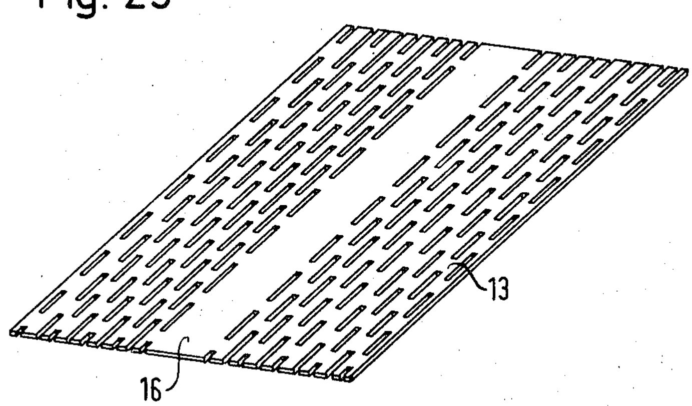


Fig. 29



ELECTROLYSIS CELL

The chlorine gas quantities developed at the anode in high current loaded alkali metal chloride electrolysis cells have to be withdrawn as quickly as possible from the electrode range for energy reasons. A stay of the chlorine gas bubbles within the electrode range will, as it is well known, bring about a considerable increase in the cell voltage and a decrease in the current output. This phenomenom which is known under the collective term "gas bubble effect" led in the last years to changes in the construction of graphite anodes. Thus, for instance, the anode plates were provided with numerous slots and gas withdrawal bores which up to current densities of $D_A = 10\ kA/m^2$ actually brought the desired success. A further increase in the current density, however, is barred by the ceramic-like graphite anode. At very high current densities, D_A in excess of $10\ kA/m^2$, it becomes difficult to sufficiently quickly withdraw the developed chlorine gas from the bottom side of the horizontal anode plate which itself is provided with rather numerous slots and gas withdrawal bores. Higher excessive voltage on the graphite and greater voltage losses in the electrolyte enriched with chlorine gas bubbles will result. Moreover, with the number of slots and gas withdrawal bores, the inner resistance increases and so does the loss in graphite and the sensitivity of the anodes during the transport thereof. Attempts have been made to circumvent these limitations by the employment of coated titanium anodes. Making use of the cell upper portion coordinated with the punch-shaped graphite anode, expensive titanium anodes are employed which, however, do not take fully into consideration the possibility of this new activated electrode material. Since, now-a-days, the current feed line and distribution of the anode is also arranged in the interior of the cell and therefore must likewise consist of resistant titanium, large quanties of this expensive material are used, which fact impedes the wide use of such anode. Moreover, maintaining the old cell upper structure and the punch-like anode shape entails drawbacks inherent to this type of construction.

In view of the numerous partially rather short life elements such as rubberized cell cover, current collecting rails, flexible current distributing cables, anode holding rods, protective tubes, sealing elements, screw and/or soldering contacts, anode suspensions and the anodes proper, the cell upper structure is very expensive and has remained complicated. Long current paths increasing the resistance, numerous contacts at the expense of the voltage and anode holding bars which impede the current feed and the current distribution while the current paths are considerably restricted by the anode holding bars hardly permit the voltage coefficient (k-value) of the electrolysis cells to drop below 0.12. In view of the rather high tolerances in dimension, as customary in the construction of cells, it is necessary that when employing titanium anodes in these cells, always an expensive time consuming and personnel intensive adjusting operation is required when assembling the metal anodes. Even the substitution of the individual anode adjustment by a motoric group adjustment has not remedied the above situation.

It is, therefore, an object of the present invention to provide a cell upper part equipped with metal anodes, in which:

1. The current feed and distribution of customary conductor material (aluminum; copper) in the form of longitudinal beams of large cross section extends to the anode proper in order to avoid a resistance increasing constriction of the current paths,
2. the quantity of titanium is limited to a minimum,
3. the anode proper is easily exchangeable,
4. the adjustment of the individual anode during the assembly becomes superfluous,
5. the spacing between the mercury cathode and the anode proper is very small and can be precisely adjusted in order to keep the voltage drop in the electrolyte very low, and
6. the overall construction will have a long life and is noncomplicated while taking into consideration all other requirements of an economic high load operation.

These and other objects and advantages of the invention will appear more clearly from the following specification, in connection with the accompanying drawings, in which:

FIG. 1 illustrates partly in view and partly in section an amalgam high load cell equipped with the cell upper part according to the present invention.

FIG. 2 shows the connection of the contact strip to the longitudinal beam by means of necked-down bolts.

FIG. 3 shows the connection of the contact strip to a U-shaped longitudinal beam by means of screws.

FIG. 4 illustrates the connection of the contact strip to the angular longitudinal beam by means of screws.

FIG. 5 shows the connection of the contact strip to the longitudinal beam from below by means of corrosion-resistant screws and seals while additionally contact-establishing means are employed.

FIG. 6 illustrates the connection of the contact strip to the longitudinal beam by means of a press fit.

FIG. 7 illustrates the connection between the longitudinal beam and the contact strip with increased contact surface while the contact is improved by a low melting alloy.

FIG. 8 shows the connection between the contact strip and the anode bars by means of clamping screws while additionally a contact-establishing means is employed.

FIG. 9 illustrates the connection of individual anode bars provided with studs to the contact strips by means of a press fit.

FIG. 10 shows the connection of individual anode bars to the contact strip by means of slotted or notched pins.

FIG. 11 illustrates the connection of individual anode bars to the contact strips by means of spring pins.

FIG. 12 illustrates the connection of individual anode bars at the rim of the contact strips by means of spring pins.

FIG. 13 shows the connection of individual anode bars to the contact strips by means of keys of durable material.

FIG. 14 illustrates the cell upper part placed upside down and equipped with anode grates.

FIG. 15 illustrates another embodiment of an enlarged contact surface similar to that illustrated in FIG. 7.

FIG. **16** shows the connection of the anode grates to the contact strip by means of slotted flat-head screws.

FIG. **17** illustrates a connection of anode grates to the contact strips by means of a press fit.

FIG. **18** shows anode grates which are arranged in longitudinal direction and are welded to the contact strips.

FIG. **19** shows an anode grate composed of parallel webs, the ends of which lead into a frame which is connected to the contact strips.

FIG. **20** shows an anode grate which is composed of parallelly arranged webs interrupted by transverse strips which are to be connected to the contact strips.

FIG. **21** shows a cutout of an anode grate forming a slotted sheet metal plate.

FIG. **22** illustrates a cutout of an anode grate forming a slotted sheet metal plate in which the webs together with the cathode form an angle of 90°.

FIG. **23** is a cutout of an anode grate in which the opening between the webs are made without losses in material.

FIG. **24** illustrates a cutout of an anode grate which represents a perforated sheet metal plate in which the bores have been produced without losses in material.

FIGS. **25** and **26** illustrate a cutout of an anode grate in which the webs and transverse strips are made from semi-finished valve metal material and are welded to each other.

FIG. **27** shows a section through an embodiment according to which the anode bars are arranged parallel to the flow direction of the mercury while the anode bars are additionally contacted by a transversely arranged auxiliary bridge.

FIG. **28** represents an embodiment of a cell upper part according to the invention with contact bolts.

FIG. **29** represents an anode grate with transverse strips, in which the gas withdrawing holes are parallel to the flow direction of the mercury.

The cell upper portion according to the present invention is characterized primarily by current feed lines and distributors which are screened with regard to the interior of the cell and which consist of conductive material as, for instance, copper or aluminum, are in the form of longitudinal beams. The cell upper part according to the invention furthermore comprises contact strips of valve metal which are arranged therebelow while a cell shielding is welded thereto, said cell shielding consisting of valve metal sheet plate material and of easily exchangeable anode bars of coated valve metal connected to the contact strips. With one embodiment employing anode grates, it may be expedient instead of the contact strips of valve metal to employ short contact bolts of the same material.

Referring now to the drawings in detail, FIG. **1** shows a cell upper portion according to the invention with an automatically adjustable supporting construction. This supporting construction comprises current conductors and distributors shielded against the interior of the cell and made of conductive material as, for instance, copper or aluminum in the form of longitudinal beams. The supporting construction furthermore comprises contact strips **2** of valve metal which are located below said longitudinal beams **1**, cell shielding means **3** welded to said contact strips **2** and made of valve metal sheet material, and also comprises anode bars **4** which are connected to the contact strips **2** and easily exchangeable while being made of coated valve metal. The cell upper part according to the invention will permit arrangement of the longitudinal beams **1** made of electrically conductive material such as aluminum or copper, at a slight distance from the anode bars **4** so that it will be possible to convey the current quantities necessary for the electrolysis, at a minimum voltage drop. The very thin contact strips **2** made of valve metal, preferably titanium do not constrict the current path and bring about considerable saving in titanium without increasing the electric resistance.

FIGS. **2**, **3** and **4**, respectively illustrate three different embodiments of the invention, and more specifically, of the longitudinal beams **1** which are made of conductive material and which make it possible from above to screw the contact strips **2** to the longitudinal beams **1**.

Another possibility consists in screwing the contact strips **2** from below to the longitudinal beams **1**, as shown in FIG. **5**. Inasmuch as with this embodiment the screws are in continuous contact with the electrolytes, they have to consist of, or be coated with corrosion resistant material, preferably valve metal and must additionally be sealed.

A further connecting possibility between longitudinal beam **1** and contact strip **2** may be effected by means of a press fit as shown in FIG. **6**.

A decrease in the transfer resistance is obtained by an enlarged contact surface between the contact strip **2** and the longitudinal beam **1**. This increase in the contact surface can be realized by a favorable configuration of the upper surfaces as, for instance, the tooth-like surface shown in FIG. **16**. The same effect may also be realized by corrugated or lamellae-like contact surfaces. According to the embodiment of FIG. **7**, the increase in the contact surface is realized by a suitable design of the screw connection.

In order to avoid or prevent an oxidation of the valve metal contact surface over a longer period of operation, it it expedient in many instances to provide the contact surface between longitudinal beams **1** and contact strip **2** with relatively precious metals and/or an oxidation impeding paste.

Primarily with the embodiments having an enlarged contact surface, with an additional contacting of the longitudinal beams with the contact strips **2** through a low melting alloy **6**, for instance, solder, a further decrease in the transfer resistance can be realized. The melting point of this alloy may also be below the temperature of operation of the electrolysis cell in order to assure a uniform filling of the hollow spaces.

FIGS. **8** – **13** show different embodiments of the connection between the contact strip and anode bars **4**. More specifically, FIG. **8** shows the connection of the anode bars in the recesses of the contact strip **2** which recesses have been prepared for this purpose. This connection is effected by means of clamping screws **8**. Further embodiments are characterized primarily in that studs or pins **9** (FIG. **9**) or slotted pins **10** (FIG. **10**) of the anode bars **4** are pressed into bores of the contact strip **2**. A very simple connection may be obtained through the intervention of explosive pins **11** (Sprengzapfen — FIGS. **11** and **12**). Hollow pins, the cavity of which is provided with an explosive charge are connected to the anode bars **4**. During the assembly, these pins are introduced into bores provided therefor in the contact strip **2.** Depending on the height of the bore in the contact strips **2,** the connection of the pin is effected either primarily by press fit as shown in FIG. **11** or by hollow rivet-like connection (FIG. **12**). As shown in FIG. **12** in connection with the embodiment having pins **11,** also the connection illustrated in FIGS. **9** and **10** on the rim of the contact strip **2** may be effected. The connection of the anode bars may also be carried out by means of keys **12** of durable materials such as valve metal or synthetic material (FIG. **13**).

The valve metal surfaces which come into contact with the cell medium passivate when used as anodes while forming non-conductive oxide layers. Contact surfaces with which a contact with the cell medium cannot be completely excluded must be protected by additional contacting means. As additional contacting means there may be employed layers of platinum metal, silver, oxidation impeding pastes, etc. These contacting means are illustrated in FIG. **8** at **7** in connection with the use of clamping screws. However, they may also be used in connection with other connecting means.

The anode rods **4** of the cell upper portion according to the invention consists of valve metal which is coated with a coat permitting an economical employment of the anode process. The term "anode bars" or "anode rods" is not limited to bars with circular cross-section, but also includes bars or rods of any desired cross-section, as for instance, square, triangular, hexagonal, rectangular, etc.

If the anode rods **4** are to be arranged so as to be parallel to the flow direction of the mercury, an additional contacting is possible by means of a transversely arranged auxiliary bridge **17** (FIG. **27**).

FIG. **14** shows a further embodiment of a cell upper part according to the invention with automatically adjustable supporting construction. Such supporting construction may consist of current conductors shielded from the interior of the cell and current distributors of conductive material such as copper or aluminum in the form of longitudinal beams **1**, contact strips **2** therebelow of valve metal, a cell shielding **3** welded thereto of valve sheet metal, and anode grates **13** of coated valve metal, which anode grates are made of valve sheet metal and are connected to contact strips **2** while being easily exchangeable. The connection between longitudinal beams **1** and contact strips **2** is expediently carried out in the same manner as described above in connection with the first embodiment of the invention.

The connection of the anode grates **13** to the contact strips **2** may be effected by a screw connection as illustrated. FIG. **16** in which instance the contact surface between contact strip **2** and anode grate **13** is additionally coated with platinum metal. As further embodiments the above mentioned connecting types by means of pins, notched pins, spring pins and keys are possible. With the embodiments comprising anode grates, considerably less connecting elements may be employed between the contact strips **2** and the anode grates **13** than is the case employing anode bars. In order, nevertheless, during operation to assure a safe and economical supply of the current to the anode grates, the contact surfaces are provided with one of the above mentioned contacting substances. A further safe supply of the current to the anode grates is assured by a metallic connection between the anode grate and the contact strip. A welding connection (FIG. **8**) is well suitable for this purpose. Inasmuch as in this instance only a few connecting points are involved, the anode grates may be exchanged by disconnecting the welding connection. This may be effected by a suitable tool, as for instance, a cutter. In order during an exchange to avoid a machining of the contact strips **2**, the webs **14** of the new anode grates are welded to the contact strip in an offset arrangement. It is for this reason that anode grates with different distances between the transverse strips **16** are prepared. In such instance only after a more frequent exchange, a post-machining of the contact strip will be necessary.

Some embodiments of the anode grates which illustrate the present invention while by no means limiting the same are illustrated in FIGS. **19 – 26.** FIG. **19** shows the embodiment of an anode grate built up of parallelly arranged webs **14** with frames **15,** whereas FIG. **20** shows an embodiment of the invention with transverse strips **16.** The connection of the anode grates **13** to the contact strips **2** by means of one of the above mentioned connections is effected on the frame **15** or the transverse strip **16.** When employing expanded metal or metal mesh as anode grate, the mechanical strength is obtained by welding to a frame **15** or from corresponding transverse strips **16** of semi-finished valve metal. Anode grates which have to be made out of a single piece are illustrated in FIGS. **19 – 24.** When the anode grates are made of valve metal sheet, the openings may be made with (FIGS. **19 – 22**), or without loss in material (FIGS. **23 – 24**). FIGS. **19 – 21** illustrate anode grates of slotted valve sheet metal. By turning the webs, considerably greater openings with the same anode surface will be obtained, which openings bring about that the chlorine gas bubbles are at an extreme speed withdrawn from the electrode range. Experience has shown that the webs should expediently form an angle of 30° – 90° with the cathode. An embodiment according to which the angle is 90° is shown in FIG. **22.** FIG. **23** shows a further embodiment of the invention with a transverse strip **16.** According to this last mentioned embodiment, the openings are produced without loss in material by bending the web edges. Also, the design of an anode grate, as illustrated in FIG. **24,** can be produced without loss in material. To this end, holes are knocked into a valve metal sheet, for instance, by means of a pointed tool without subsequently deburring the holes. It is, of course, to be understood that instead of this metal sheet also a commercially obtainable perforated sheet may be employed which is provided with transverse strips for assuring mechanical strength.

FIGS. **25** and **26** illustrate anode grates **13,** the webs **14** and transverse strips **16** of which consist of semi-finished valve metals which are welded to each other. In the same manner, it is also possible to produce anode grates **13,** the webs **14** and frame **15** of which, consists of weldable semi-finished valve metals.

All above described anode grates may be provided with a coat or layer, either on one side or also on both sides, said coat or layer being adapted to permit an economical carrying out of the anode process.

For purposes of enlarging the "true anode surface," the webs of the anode grates may entirely or at least at their surface consist of sintered activated valve metal and may be welded to the frame or transverse strip.

FIG. **28** shows a third embodiment of the cell upper part for amalgam high load cells with conductors shielded relative to the interior of the cell and with current distributors of conductive material such as copper or aluminum in the form of longitudinal beams **1**, contact bolts **2**a arranged therebelow and consisting of valve metal, a cell shielding **3** welded thereto and consisting of valve metal sheet, and easily exchangeable anode grates **13** of coated valve metal, said anode grates **13** being connected to the contact bolts **2**a. The connection between longitudinal beam **1** and contact bolts **2**a, or contact bolts **2**a and an anode grate **13** is carried out expediently in the same manner as described in connection with the above mentioned embodiments. This embodiment with contact bolts **2**a results in a further saving of valve metal and thereby brings about a reduction in costs of manufacture. Due to the great conductor cross-section of the contact bolts **2**a, with this embodiment the increase in cell voltage is immaterial in view of the unavoidable constriction of the current path. The anode grates **13** are designed in the same manner as described above in connection with the second embodiment of the invention.

With the two embodiments of the cell upper part according to the invention with anode grates **13**, the webs **14** of the anode grate **13** may be arranged transverse or parallel to the direction of flow of the mercury. The arrangement and design of anode grates with fram according to which the webs are parallel to the direction of flow of the mercury is shown in FIG. **14.** The design of anode grates according to which the webs extend transverse to the direction of flow of mercury is shown in FIG. **19** in connection with an anode grate comprising a frame **15** and in FIGS. **16** and **20** in connection with an anode grate having a transverse strip **16.** FIG. **29** shows an anode grate **13** with transverse strips **16,** the webs **14** of which, are parallelly arranged with regard to the direction of flow of the mercury.

With the cell upper part according to the invention, the current conductors and distributors are made of a very good conductive material such as copper or aluminum whereby a considerable quantity of titanium is saved. By employing the considerably cheaper and better conductive materials, it is economically possible to dimension the conductors and distributors more generously. In view of the more generous dimensioning of the conductor cross section and in view of the short distances from the anode proper, it is possible with these cell upper portions to obtain an excellent voltage coefficient. The better the voltage coefficient, the lower the costs of operation will be.

With all embodiments of the cell upper part according to the invention, due to the construction according to the invention an excellent plane parallelity of the anode surfaces will be realized. In view of the plane parallelity, a minimum spacing between the mercury cathode and the anode will be possible which, in turn, brings about a very slight voltage drop in the electrolyte. This plane parallelity of the anode surface will be maintained also when exchanging the anode bars or anode grates because during the assembly of the exchange anodes the connecting members thereon will engage recesses of the contact strip or contact bolts provided therefor, so that an automatic adjustment of the anode surface will be obtained. The expensive and time consuming adjusting operation with the heretofore known assembly of metal anodes will therefore be completely eliminated when employing the cell upper part according to the invention. In spite of the said expensive adjustment with heretofore known plunger anodes it was difficult with such anodes to maintain plane parallelity during the entire operation. Plane parallelity of the anode surface is, however, one of the most important requirements for a safe operation of amalgam cells because unevenness of the anode surface frequently causes short circuits.

The anode bars and anode grates of the cell upper part according to the invention are washed around from all sides by the electrolyte and, therefore, the electrolysis process may occur on the entire coated surface of the anodes, As a result thereof, with equal space requirement an increase in the production capacity is possible.

The construction of the cell upper part according to the invention makes it possible so to design the anode bars or anode grates that the developed chlorine gas can be withdrawn in a minimum of time from the range of the electrodes. In this way, the undesired influence of the so-called gas blowing effect will be impeded to a major extent.

Due to the far reaching replacement of the valve metal required for current feeding and distribution by considerably cheaper conductive material such as copper or aluminum, considerable quantities of titanium are saved and thus the investment costs are considerably lower. A source of disorder in the heretofore known cell upper part is formed by the numerous seals which are required in the cell cover and which have to be continuously served and checked. With the construction according to the invention, such or similar wearing elements are not required. Consequently the overall structure of the cell upper part according to the invention for amalgam heavy duty cells has a long life, is not complicated and therefore meets all requirements of an economic heavy duty operation.

It is, of course, to be understood that the present invention is, by no means, limited to the particular showing in the drawing but also comprises any modifications within the scope of the appended claims.

What is claimed is:

1. A cell upper part formed by a top electrode structure for amalgam heavy duty cells including spaced longitudinal beams of a metal selected from the group consisting of copper and aluminum, contact elements of valve metal secured in electrical contact to the bottom surface of said longitudinal beams, shielding means of sheet valve metal extending between said beams and all of said contact elements and secured to said elements in fluid tight contact and closing off said longitudinal beams from the cell contents below said beams, and a grate structure of valve metal having spaces therethrough extending below said beams and secured in electrical contact to said contact elements of valve metal, so that the contact elements and shielding means provide barrier means to protect the electrically conducting beams from the cell gases.

2. A top electrode structure as claimed in claim **1,** in which said contact elements are strips secured to the bottom surfaces of said beams.

3. A top electrode structure as claimed in claim **1,** in which said grate structure is formed of coated valve metal.

4. A top electrode structure as claimed in claim **1,** in which said contact elements are made of titanium.

5. A top electrode structure as claimed in claim 1, in which the contacting surfaces between said beams and contact elements are formed of a precious metal.

6. A cell upper part in combination according to claim 2 in which screw means are provided to fasten said contact strip elements to said longitudinal beams.

7. A cell upper part in combination according to claim 2 in which press fit means are provided to fasten said contact strip elements to said longitudinal beams.

8. A cell upper part in combination according to claim 2 in which the contacting surfaces of said longitudinal beams and contact strip elements are corrugated.

9. A cell upper part in combination according to claim 1 in which said contact elements on beam side thereof have contact material coating.

10. A cell upper part in combination according to claim 2 in which recesses are provided on the bottom side of said contact strip elements, and anodes in form of bars are clamped by screws into the recesses.

11. A cell upper part in combination according to claim 2, in which contacting means including a coating of oxidation-retarding paste and the like is provided between said contact strip elements and the anodes.

12. A cell upper part in combination according to claim 1, in which said contact elements are welded together with the anodes.

13. A cell upper part in combination according to claim 1, in which there are anode grates providing webs arranged in parallel, and a frame means into which ends of the webs pass, said frame means being fastened to said contact strip elements.

14. A cell upper part in combination according to claim 13 in which transverse strips interrupt the webs and are fastened to said contact elements.

15. A cell upper part in combination according to claim 14 in which the webs and frame means are made in one piece.

16. A cell upper part in combination according to claim 1 in which anode grate structure consists of slotted plate material.

17. A cell upper part in combination according to claim 1 in which anode grate structure consists of expanded metal.

18. A cell upper part in combination according to claim 13 in which the webs on the upper surface thereof consist of sintered valve metal.

19. A cell upper part in combination according to claim 13 in which the webs of the anode grates are arranged transverse to said longitudinal beams.

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