Oct. 1, 1968 M. S. KIRCHER 3,404,083

CYLINDRICAL ANODE ELECTROLYTIC STRUCTURE

Filed Nov. 30, 1966 6 Sheets-Sheet 1

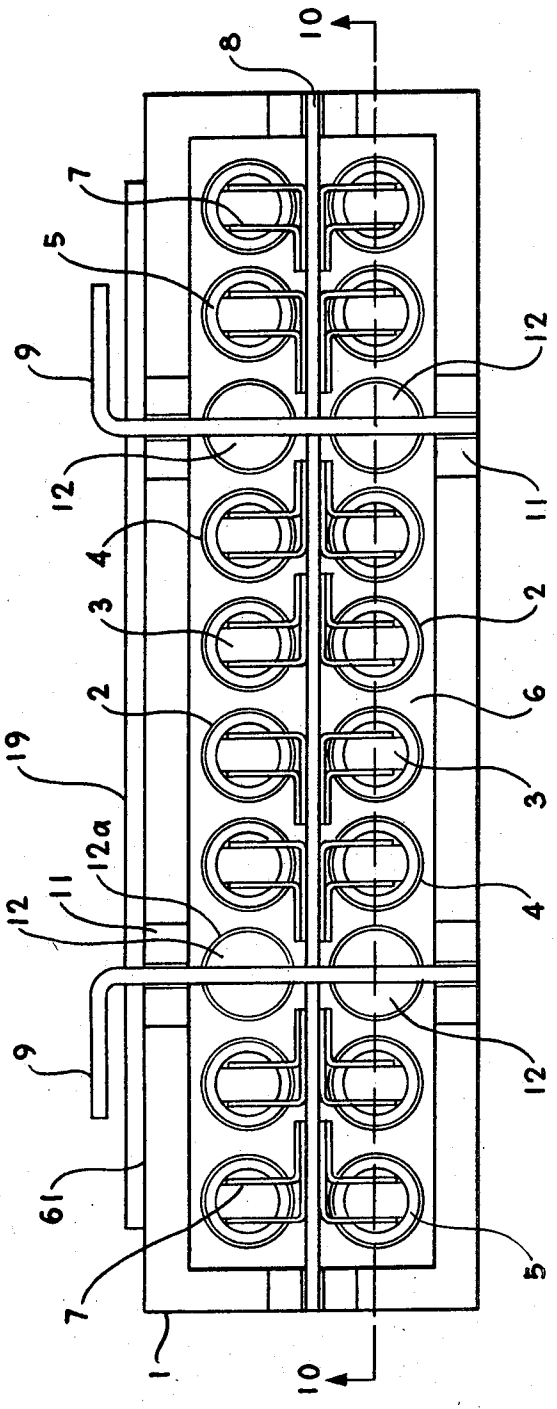


Fig. 1

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CYLINDRICAL ANODE ELECTROLYTIC STRUCTURE

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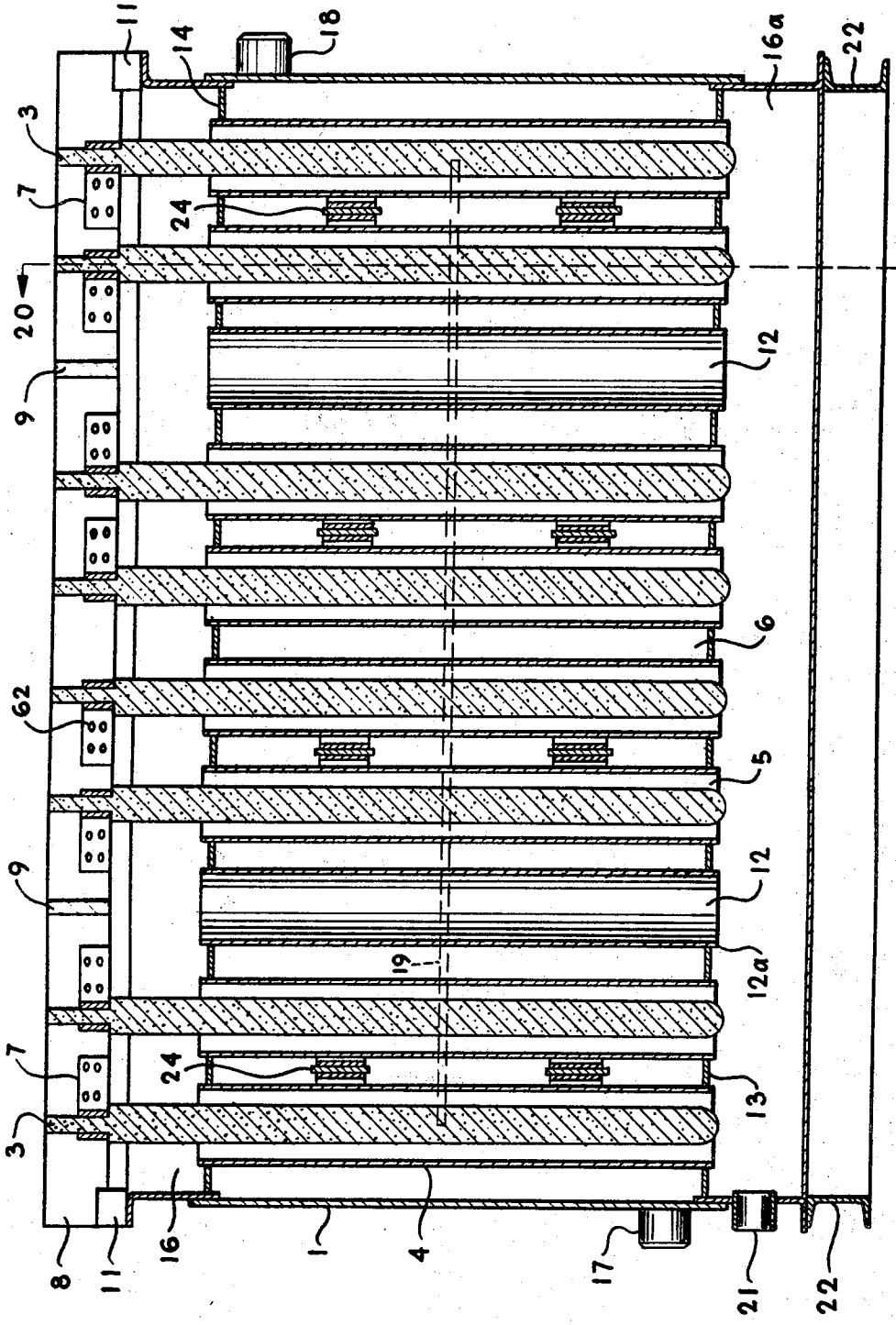


Fig. 2

CYLINDRICAL ANODE ELECTROLYTIC STRUCTURE

Filed Nov. 30, 1966 6 Sheets-Sheet 3

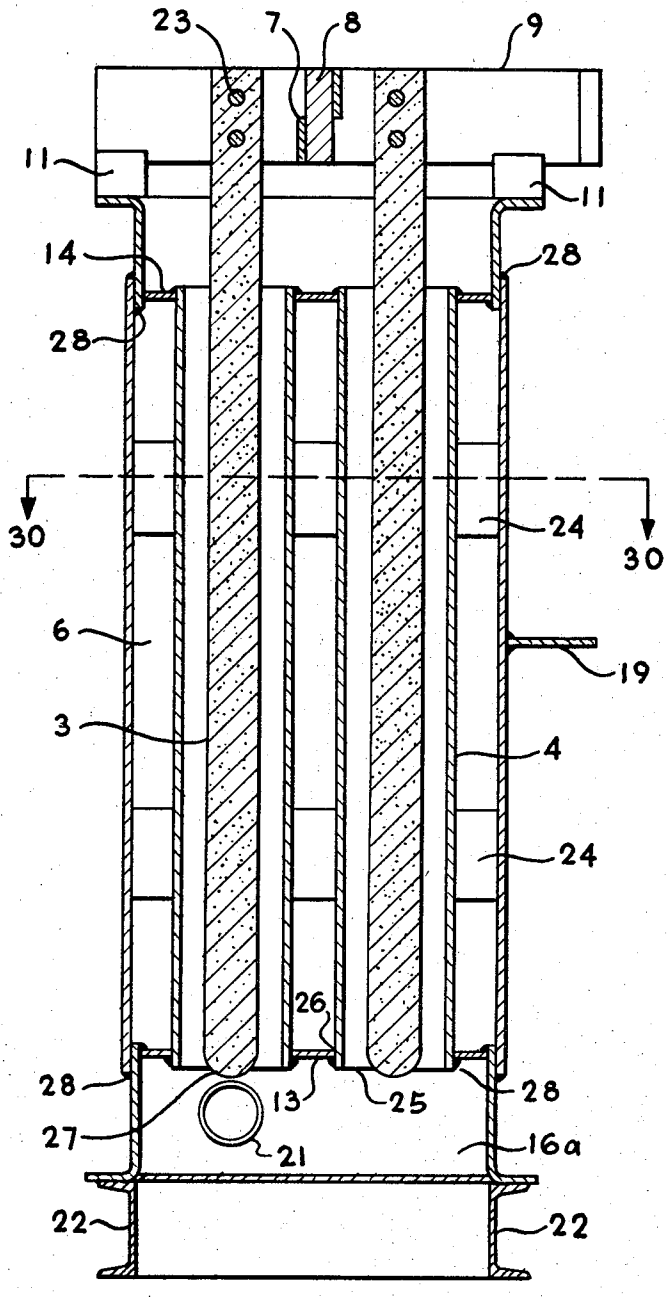


Fig. 3

CYLINDRICAL ANODE ELECTROLYTIC STRUCTURE

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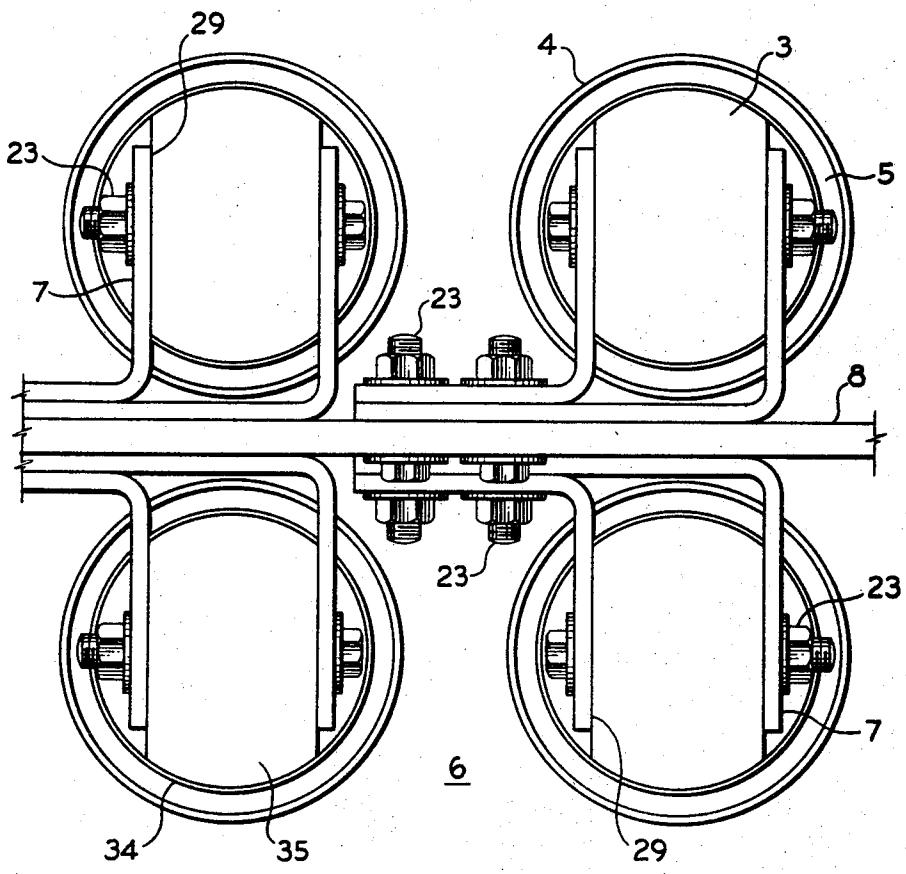


Fig. 4

CYLINDRICAL ANODE ELECTROLYTIC STRUCTURE

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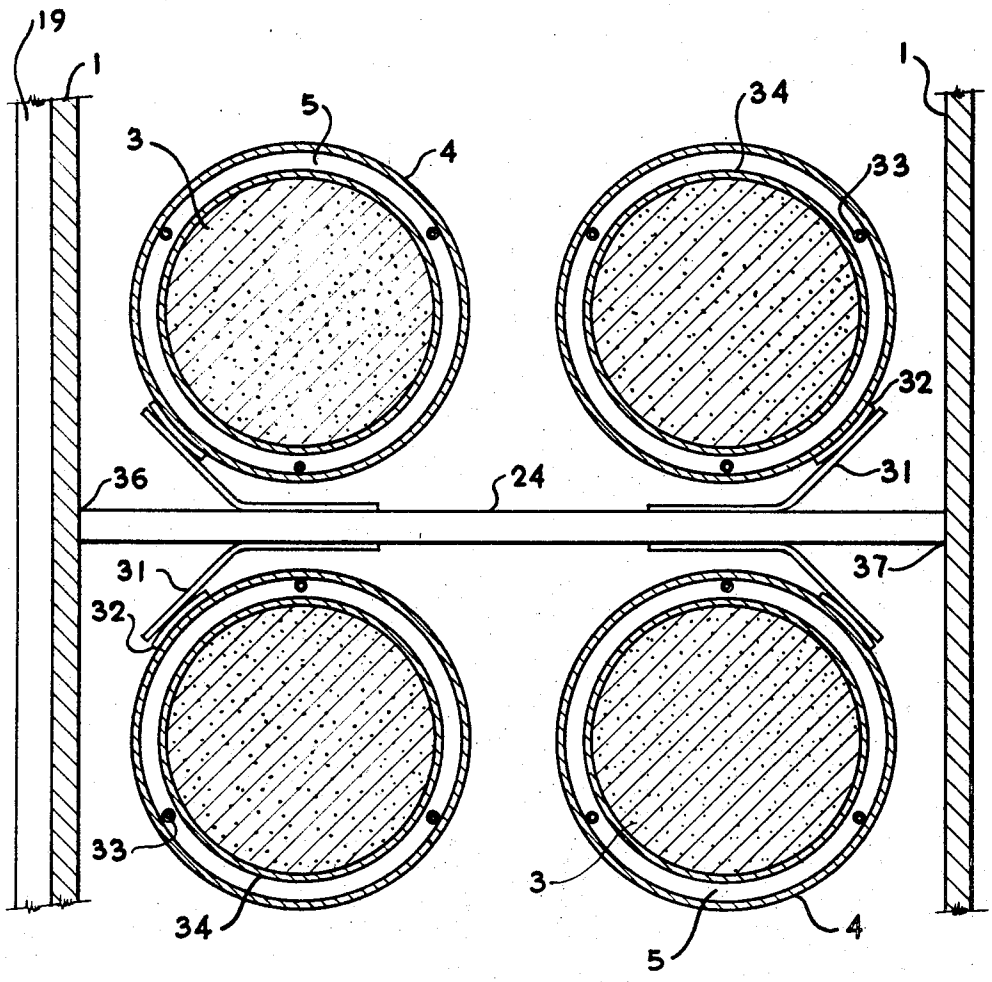


Fig. 5

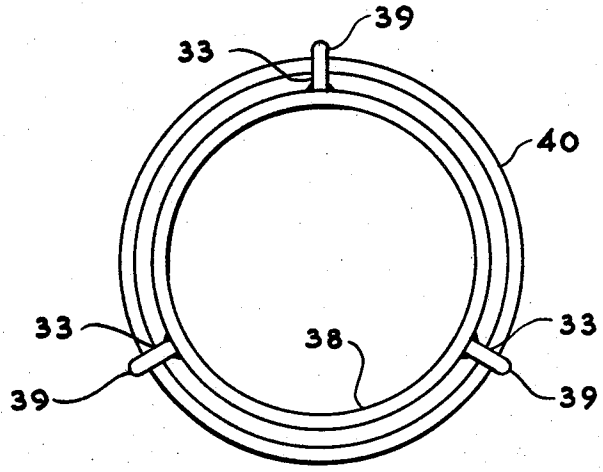


Fig. 7

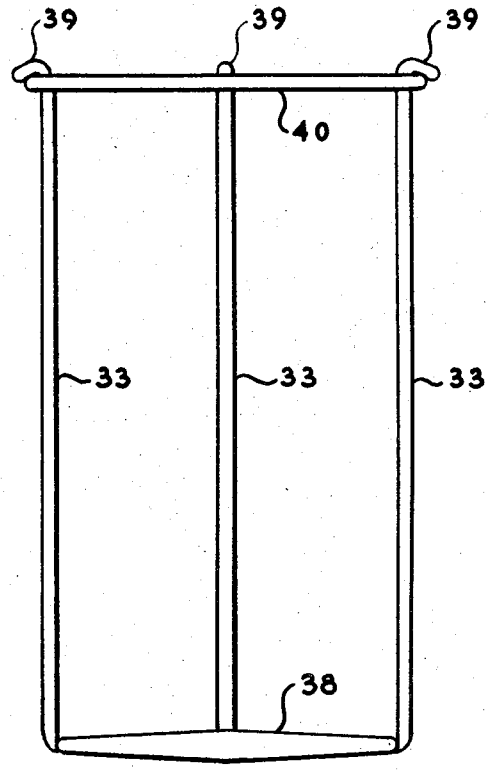


Fig. 6

United States Patent Office 3,404,083 Patented Oct. 1, 1968

3,404,083

CYLINDRICAL ANODE ELECTROLYTIC STRUCTURE

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Continuation-in-part of application Ser. No. 130,516, Aug. 10, 1961. This application Nov. 30, 1966, Ser. No. 607,104

3 Claims. (Cl. 204—272)

ABSTRACT OF THE DISCLOSURE

Electrolytic cell for the production of perchlorates and the like, having cylindrical cathode tubes vertically positioned within and extending through a heat exchanging shell. Rod-like anodes having a soft surface, such as a layer of crystalline PbO_2 deposited on a graphite base are detachably and adjustably suspended in the cathode tubes. The electrolyte chamber extends above and below the shell. Downcomers like empty cathode tubes provide for electrolyte circulation and conductor bars inside the shell supplement cathode current flow.

This is a continuation-in-part of Ser. No. 130,516, filed Aug. 10, 1961, now abandoned.

This invention relates to an electrolytic system using a cylindrical anode. More specifically, the inventive concept resides in a cell structure having a PbO_2 coated cylindrical anode adapted for use in the electrolytic production of perhalates, perchlorates, chlorates and the like, from aqueous alkali metal and alkaline earth metal halides, hypohalides and halates.

Generally, the conventional prior art cells used in the production of the above-indicated products comprise a plurality of rectangular shaped electrodes juxtaposed in relation to each other. While there is a somewhat general use of these electrodes, there are certain inherent limitations in the commercial use of same, especially when used in elevated temperature systems. One of the most undesirable of these disadvantages is the cracking and decomposition of these rectangular electrodes. During the electrolytic process certain mechanical stresses are imparted on these electrodes from forces caused by penetration of electrolyte into the graphite and stresses due to differences in coefficients of expansion subjected to temperature changes. Especially of interest is the graphite base type of electrode having thereon a coated active material such as lead dioxide. While the coated active material is substantially impervious to anodic corrosion, the graphite base is corrodible, and will decompose upon contact with the electrolyte. It is therefore, desirable to retain the coated active material thereon without any breaks, cracks, or openings. In the rectangular type electrode, because of the configuration of same, it is not uncommon for breaking or cracking to occur in the coated active material. The corner areas in particular are susceptible to cracking caused by the opposite pressures imparted on the adjacent perpendicular side portions of the rectangular electrodes. Once the coated active material is cracked, the inner base graphite material becomes exposed to the electrolyte of the system and thereby corrodes upon attack by the electrolyte. As the base graphite material expands, the stresses exerted on the lead dioxide plating are substantially greater at the corner portions, thereby resulting in breaking of the plated material at these areas. By constructing the electrodes in a cylindrical fashion, there is substantially less, if any, occurrence of fractures due to internal expansion of the graphite base material. A further advantage of the cylindrical type electrode is that it exposes the surface of the active material more uniformly to electrolytic action than a rectangular electrode.

Other types of anodes generally in use presently in systems of this type are platinum wire or platinum foil electrodes. The comparatively high price of said platinum electrodes restricts the desirable commercial use of same. Thus, in the electrolytic manufacture of halates, perhalates, perchlorates, and the like, there has been a need for improved, longer life electrodes, together with electrodes of substantially lower initial cost and maintenance. The cylindrical shaped graphite base-lead dioxide plated electrode provides an electrode of comparatively low cost, one easily produced, and one substantially overcoming the apparent drawbacks of the above-discussed prior art electrodes. Generally known methods for producing graphite coated-lead dioxide plates, such as that shown in U.S. 2,945,791 to F. D. Gibson, Jr., may be used to make the anode used in the cell of this invention. However, maximum advantage of these electrodes has required a completely new concept in cell construction and design, one specifically intended for incorporation of this type electrode.

Recent advances in the art have provided somewhat cylindrical shaped anodes generally constructed of a graphite base having thereon a plating or coating of electrolytically active lead dioxide. This type of structure provides an electrode of comparatively low cost, one easily mass produced, and one substantially overcoming the apparent drawbacks of the above-discussed electrodes. To utilize such an electrode efficiently, presently available cell structures had to be redesigned, modified, or readapted for this specific electrode. However, maximum advantage of these electrodes has required a completely new concept in cell construction and design, one specifically intended for incorporation of this type electrode. This invention includes a cell construction especially adapted for this cylindrical electrode. To facilitate this end, it was required that a cell be constructed having a high rate of electrolyte circulation, low initial investment and maintenance costs, effective cell cooling means, and high operating efficiency.

The cell of this invention comprises a shell box-like container and a heat exchanger that is integral therewith. Provided in the inner portion of said shell is a plurality of vertically positioned or downwardly extending tube means open at the upper portion, most of which are adapted to be cathodes and to receive and house the above-mentioned cylindrical anodes. The remainder of the tube means are adapted to be downcomers for electrolyte circulation. The cell structure provides for each of said cylindrical anodes to be independently suspended in said cathode tube means, thereby enabling easy and convenient insertion and removal. Around the outer peripheral portion of said anode and intermediate said anode and said cathode tube means is positioned an electrolyte chamber adapted to provide easy access and contact of anode to said electrolyte. The tubular means generally are constructed of stainless steel or other suitable materials.

Encircling the outer portion of said cathode tubes and downcomer tubes is a water jacket constructed in such a manner as to provide free circulation throughout the system. By integrating this heat exchanger within the cell, savings in investment and pump costs are realized, while providing a superior, well functioning cooling system.

As mentioned earlier herein, the cylindrical anodes avoid cracking and nonuniform wear. The cylindrical or tubular shaped cathodes are desirably inexpensive while providing the optimum space arrangement with the specifically designed anode means.

Extending longitudinally across the upper portion of

said cell is a conductor bar (usually copper or some other suitably conductive material), contacting each anode means in a parallel fashion. This conductor bar provides the positive lead or source of energy. Below the upper horizontal level of said anodes is positioned a second conductor bar which contacts each cathode in a parallel fashion; this conductor provides the vehicle through which the negative charge is transferred from one cell to the other.

The downcomer tube means discussed above provides highly efficient circulation throughout the multiple cell structure. Above and below the terminal portions of the electrodes are provided electrolyte chambers in open communication with the electrolyte chambers between the electrodes, insuring a constant and sufficient amount of electrolyte to be supplied to the vertically extending annulus-like electrolyte chambers formed by said cathode tube means and anode tube means. The lower electrolyte chamber acts as a product collection chamber. Adjacent to and integral with the end portion of said product collection chamber is situated a product outlet means. This outlet means extends from the internal portion of said product collection chamber to the atmosphere. The upper top structure which defines the upper partition of said product collection chamber is provided with a plurality of apertures or openings adapted to receive and support the lower terminal portion of said cylindrical anodes. Situated at the lower side of the rectangular shell container is a water inlet means adapted to contact and receive a water source means, and feed a somewhat constant supply of water throughout the system. Situated above the horizontal plane of said water inlet means is a water outlet through which the water passes out of the cell system.

The invention will be defined in greater detail in relation to the accompanying drawings.

An object of this invention is to provide a cell wherein the anode and adjacent electrolytic elements are constructed in such a manner that a substantially even stress is imparted throughout the surface of said anode during operation.

It is a further object of the present invention to provide a cell structure adapted to efficiently utilize the cylindrical type anode.

It is another object of this invention to provide a cell having desirable electrolyte circulation wherein the electrodes are easily contacted by said electrolyte.

Another object is to provide a cell structure having tubular-like chambers therein adapted to house a complete unit cell.

Still another object is to provide a cell structure with an integral heat exchanger, thereby avoiding the necessity of additional elements in operating the system.

A yet further object is to provide a cell housing structure having convenient anode insert, removal, and adjustability means therein.

Additional objects will be apparent to those skilled in the art from this detailed disclosure.

The following drawings illustrate a preferred embodiment of this invention. It should, however, be understood that the drawings merely illustrate one embodiment of the present invention and are not meant to limit the invention to the specifics set out therein. Although graphite and lead dioxide are discussed as the components of the electrode, it is within the scope of this invention to use other suitable cylindrical anode materials.

FIGURE 1 illustrates a top plan view of the structure of the cell of this invention.

FIGURE 2 illustrates a sectional view of this cell taken along lines **10—10** of FIGURE 1.

FIGURE 3 illustrates a front sectional view of the cell of this invention taken along lines **20—20** of FIGURE 2.

FIGURE 4 illustrates an enlarged top view of a cell of this invention showing the specifics of the anode electrical connections.

FIGURE 5 illustrates an expanded cutaway view taken along lines **30—30** of FIGURE 3, and illustrating the cathode electrical connections.

FIGURE 6 illustrates a preferred form of guide and support means for positioning a unit cylindrical anode inside a unit cathode tube.

FIGURE 7 shows a top view of the guide and support means illustrated in FIGURE 6.

Referring first to FIGURE 1, shell container **1** houses a plurality of unit cell opening structures **2**. Shell **1** may be constructed of any suitable metal, such as stainless steel, or the like. The cell openings **2** and **12** are shown as being arranged in two aligned parallel rows extending longitudinally through the shell **1**. These cell openings **2** and **12**, however, could easily be arranged in staggered positions if desired, and/or in as many longitudinally disposed rows as required. Suspended in cell openings **2** are the cylindrical anodes **3** to be used in the cell structure of this invention extending vertically downwardly through substantially the depth of the shell container **1**. Encircling the anodes **3** are cathode structures **4**. As above-discussed, the graphite anodes having thereon a coating of lead dioxide are ideally utilized in the structure of this invention. However, it would not depart from the scope of this invention to use other type anodes herein with the cell structure of this invention. The cathode preferably is constructed of stainless steel, or copper or nickel; however again, change in composition of this cathode would not depart from the inventive concept herein defined.

Intermediate the anode **3** and the cathode **4** and defined thereby is an electrolyte chamber **5**, preferably extending at least the vertical depth of the cathode **4**. It is conceivable, however, that the electrolyte chamber may in a given situation be more desirably situated whereby something more or less than the vertical depth of the cathode **4** is encircled or enclosed.

Intermediate each cell opening **2** is situated a water chamber **6** which extends both laterally and longitudinally throughout substantially the shell container **1**. This water chamber **6** acts as a heat exchanger or cooling means whereby a somewhat even and constant temperature is provided throughout the entire system. Any suitable liquid cooling means may be utilized if convenient and desired.

Attached to and providing support for the anodes **3** are electrical conductor leads **7** which supply the source of current to the system through the anodes **3** Centrally located intermediate the aligned rows of cell openings **2** is an anode conductor bar **8** which is connected to an electrical source of direct current energy (not shown in drawing), and provides this same energy directly to the unit cells through conductor leads **7**. Both the anode conductor bar **8** and leads **7** may be constructed of any suitable material, the preferred substance, however, is copper. Each lead **7** is secured to the top terminal portion of the anode **3**, thereby providing a fixed but adjustably spaced relationship between the anode **3** and cathode **4**, and also providing sufficient passage means through which the electrolyte may flow.

It has been found that bolt means, rivet means, adhesive means, and other known removable connectors may be used to secure the leads **7** to the anodes **3**. I prefer to provide the means for securing the anodes **3** to the anode conductor bar **8** with a certain amount of adjustability so that each anode **3** can be individually adjustably positioned within its cathode tube **4**. One method for providing for this is to have bolt holes (shown in FIGURE 2 as numeral **62**) in the anode leads **7** be oversize with respect to the bolts, and even more preferably oversize and elliptical in shape.

The choice of electrolyte utilizable in this cell is a matter of choice, design or expediency; however, since the present structure is ideally adapted for use in the production of sodium perchlorate, a sodium chlorate electrolyte

would be desirably employed. It is to be understood, however, that other electrolytes can also be used in the electrolytic cell of this invention. For instance, the cell can be used in the production of potassium perchlorate from potassium chlorate. It can also be used to electrolyze other alkali metal halides, halates and hypohalides, such as lithium chloride, and to electrolyze alkaline earth halides, halates and hypohalides, such as calcium chloride and magnesium chloride. Another halogen to be included is bromine.

Supplying current to the conductor bar **8** is any suitable wire or current carrier **9**. Insulating current carrier **9** from the side structures **10** is insulating means **11**; any suitable insulating materials such as rubber, plastics, or other synthetics or mixtures thereof not readily attacked by the electrolyte, including perchlorates, may be used.

The top face portion of shell container **1** may preferably be open to allow easy access to the anodes and other elements for removal, insertion or repairs. However, a cover means can be used to close the top if desired.

It will be noted that in the preferred embodiment, some cell openings **12** (downcomer tubes **12***a*), are left unfilled, thereby providing better electrolyte circulation throughout the system. These downcomer tubes provide excellent return circulation. The downcomer tubes **12***a* are preferably constructed of stainless steel, copper or nickel; however, again change in composition of the downcomer would not depart from the inventive concept herein defined. The cross-sectional size and shape of the downcomer tubes **12***a* are preferably the same as the cathode tubes **4**; however, other cross-sectional sizes and shapes can be used. The downcomer tubes **12***a* are not provided with internal conductor bar means, which are provided for the cathode tube means **4**, because they are not being used as cathodes. Also, ample space at the top and bottom of the cell provides rapid electrolyte circulation which promotes high current efficiency and low voltage.

FIGURE 2 illustrates a side view taken along lines **10—10** of FIGURE 1. Downwardly extending anodes **3** project from leads **7** through the length of the vertical cylindrical cathode tubes **4** to bottom wall structure support **13**. Immediately adjacent the anodes **3**, and encircling substantially the length of same is an electrolyte chamber **5**. Downcomer tubes **12***a* also are positioned in the cell to form therein cell opening **12**. Somewhat sinusoidally disposed to the center axis of said cell openings **2** and **12** is the water jacket or chamber **6**, having a bottom closure wall **13**, and a top closure wall **14**. Above and below said electrodes are positioned additional electrolyte chambers **16** and **16***a*, respectively, thereby insuring somewhat constant flow of electrolyte through the vertically disposed electrolyte chambers **5**. The electrolyte flows through the vertical length of the electrolyte chambers **5** and through chambers **16** and **16***a*, so that cathode tubes **4** and end closures **13** and **14** serve as heat exchange walls of water jacket or chamber **6**. The optimum cooling effect on the electrolyte is thereby provided. The electrolyte may be fed to the system through the open top portion of the cell or through an inlet means (not shown), if desired. It is preferred that the top be used so that the electrolyte level may be easily determined and viewed. At the lower portion of the shell container **1** is located a cooling water inlet means **17**, through which the water is fed to the system from any convenient source. On the opposite end face is situated a water outlet means **18**, by which the water may leave the system or be recycled throughout.

Extending horizontally across substantially the length of the outside of the shell box-like container **1** is a cathode conductor bar **19** which is in electrical communication or contact with the cathodes **4** of the system through the shell **1** and bottom closure wall **13** and top closure wall **14**. Intermediate the cathodes **4** and said conductor bar **19**, are cathode leads **31** (shown in FIGURE 5) and cathode connectors **24**. The cathode connectors and cathode leads provide internal means for transfer of electrical current between the cathode tube **4**, the shell and conductor bar **19**, at a position or positions intermediate or between the upper terminal portion and lower terminal portion of each cathode tube where the top and bottom closure walls of the shell surfaces **14** and **13**, respectively, are in electrical communication with the cathode tubes.

The product manufactured, such as sodium perchlorate, would collect in the vertical and bottom electrolyte chambers **16***a* and be withdrawn through product outlet means **21**.

The complete shell container **1** may, if desired, be supported by a support **22**, thereby affording longitudinal strength across the bottom portion of the bottom chamber **16***a*. Anode securing means at the top terminal portion of each anode **3** are partially illustrated at **23** (shown in FIGURE 3); it is preferred that nut and bolt means be used herein to provide convenient adjustability and release means when it is desired to adjust or remove said anodes from the cell. The bolt holes **62** in the anode leads are oversize with respect to the bolt diameter, to provide for fine adjustable positioning of the anodes **3** within the cathode tubes **4**.

FIGURE 3 illustrates a front view taken along the lines **20—20** of FIGURE 2. At **24**, two cathode connectors and wall support means are indicated. These connectors not only retain a fixed degree of separation but also provide electrical contact between the cathodes **4** and the shell container wall **1**, in addition to the electrical contact provided through bottom closure wall **13** and top closure wall **14**. The shell **1** is adapted to be in electrical communication with a cathodic source of electricity through cathode conductor bar **19** horizontally attached to the shell midway between the top and bottom of the cathode tubes **4**. The upper wall **13** of bottom electrolyte chamber **16***a* is privided therein with a plurality of apertures **26**, receiving the bottom terminal portion **25** of each cathode structure **4**. The terminal portion **25** of each cathode structure is adapted to receive and support the bottom terminal portion **27** of anodes **3**. Product outlet means is provided at **21**, extending from the peripheral portion of electrolyte chamber **16***a* through to the atmosphere. Center conductor bar **8** is illustrated intermediately positioned between the top terminal portions of the anodes **3**. Water jacket **6** is shown sealed to prevent any leakage or dilution of the electrolyte. Sealing means **28**, such as solder, plastics, welded materials, and the like, can conveniently be utilized for this purpose. Cylindrical shaped anodes **3** may be tapered or squared at the upper terminal portions (as shown in FIGURE 4) so as to have at least two plane sides and to provide for more convenient and expedient attachment to leads **7**.

FIGURE 4 illustrates an enlarged top view of the anode connection means. Anode **3** comprises base portion **35** and plated portion **34**, and is substantially squared off at top portion **29**, to thereby be more conveniently secured to leads **7** by securing means **23**. Securing means **23** preferably are nut and bolt means, easily locked and unlocked in position. Cathodes **4** are shown encircling anodes **3**, thus forming a convenient electrolyte chamber **5** between each anode and cathode. Below, and on a lower horizontal plane from the horizontal plane of the anode leads **7**, is positioned cathode connectors **24** (as shown in FIGURE 5 with corresponding lead connectors **31**).

FIGURE 5 is a top cross-sectional view taken along lines **30—30** in FIGURE 3, and illustrates the means by which electrical communication is made internally between the cathodes **4** and the cathode conductor bar **19**. Cathode connector and wall support means **24** pass intermediate any two parallel rows of cell cathode tubes **4**. Connecting the cathode connectors **24** to the cathode tubes **4** are cathode leads **31**, which are in electrical and physical contact with cathodes **4** at a point indicated at **32**. These cathode leads **31** are preferably positioned on a horizontal plane approximately midway between the upper terminal portion and lower terminal portion of shell

container **1**, however, may suitably be positioned at any portion below the horizontal plane of said anode leads. As shown in FIGURE 2, it is preferred to have two cathode connectors **24** providing internal electrical communication to the cathode tubes. However, one or more than two cathode connectors spaced intermediate the top closure wall **14** and the bottom closure wall **13** of the cell may be used. The cathode connectors **24** are in physical and electrical communication with outside shell wall **1** at **36** and **37**. The outside shell wall **1** in turn is in physical and electrical communication with the cathode conductor bar **19**.

Guides **33** may be provided to insure a fixed vertical positioning of said anodes **3**, downwardly through the depth of the cell opening **2** into the cathode tubes **4**. These guides may extend vertically through the length of said cell openings **2** or may be positioned on various areas on the peripheral portion thereto.

FIGURE 6 illustrates a preferred means for independent positioning of the cylindrical PbO_2 coated graphite anodes **3** in the cathode tubes **4**. Nonconductive rod-like guides **33** are secured at one of their ends to a non conductive, substantially circular ring **38** of area somewhat less than the cross-sectional area of the anodes **3**, and at the other of their ends are formed into outwardly directed hooks **39**. Nonconductive, substantially circular slip ring means **40** of inside diameter greater than circular ring **38** and anode **3** is provided to be slipped over the guides **33** after the bottom terminal portion **27** of anode **3** is placed against the ring **38** within the guides. Then the anode with its terminal end **27** placed against the ring **38** and guide means **33** resting along the cylindrical surface of the anode **3** can be inserted into the cathode tube **4**, as a unit, with the slip ring **40** and/or hooks **39** on the guide members **33** acting to hold the anode **3** in the tube and prevent it from dropping through into the lower electrolyte chamber **16***a*. Although ring **38** is depicted as substantially circular in FIGURE 6, it is not essential that it be this shape. For instance, where three guides **33** are used, it may be preferable to use a triangular shaped ring. Its area of course would still be less than the cross-sectional area of the cylindrical anode. While I prefer to use the slip ring **40** in connection with the guide means **33**, it is not necessary. The hooked ends **39** of guides **33** may be sufficient. The guide and positioning means **33**, **38** and **40** may be fabricated from any of the known nonconductive chemically resistant materials, such as polyvinyl chloride. This guide and support means provides a method for inserting and positioning each anode in its cathode tube with substantially no injury to the delicate surface of the anode.

While I prefer to use the anode guide and support means illustrated in FIGUURE 6, it is to be understood other guide and support means may be used which enable substantially no injury to the surface of the anode, without departing from the scope of this invention. One such alternative is shown in FIGURE 3 where the anode **3** is supported on its terminal end **27** by nonconductive members supported by the terminal end **25** of the cathode tube **4**. One embodiment of such support member is to provide a nonconductive ring, similar to ring **38** shown in FIGURE 6, for positioning the terminal end **27** of anode **3**, and centrally position this ring **38** in the terminal end **25** of each cathode **4**, by positioning means, such as by nonconductive arms affixing the ring **38** with the terminal end **25** of cathode **4**. The centrally positioned nonconductive ring would then act as positioning and support means for the anode **3**.

Although this invention has been described in relation to the production of perhalates, and in particular sodium perchlorate, it would be a mere matter of choice to adapt it for other production systems. Specifics given herein are for the purposes of illustration, and are not meant to restrict the invention.

I claim:

1. In an electrolytic cell comprising: (1) cylindrical cathode tube means vertically positioned within and extending through a heat exchanging shell container means at both ends of said tube means and having electrical connection means for said cathode tube means; (2) cylindrical anode means vertically positioned within said cathode tube means; (3) electrical conduction means connected to the top portion of said anode means; and (4) electrolyte chamber means above and below said shell container means, said electrolyte chamber means being in open communication with the annulus provided by said cathode tube means and said anode means, and having electrolyte inlet and outlet means therefor, the improvements which comprise: (A) electrolyte downcomer means vertically positioned within and extending through said heat exchanging shell container means at both ends; (B) cathode internal conductor bar means within said heat exchanging shell and in electrical communication with the cathode tube means and said heat exchanging shell between the upper terminal portion and the lower terminal portion of the said shell container means; and (C) anode lead means detachably connected to said electrical conduction means and to said top portion of said anode means and adapted for adjustably positioning the said anode means in the said cathode tube means.

2. The improved cell of claim **1** comprising, in addition, nonconductive positioning and support means for independent positioning of each cylindrical anode means in each cathode tube means.

3. The improved cell of claim **2** wherein the positioning and support means comprising nonconductive rod-like guides secured at one end to a nonconductive ring of area somewhat less than the cross-sectional area of the said cylindrical anode means, and formed at the other end into outwardly directed hooks, whereby the terminal end of the anode means is placed against the said ring and the guides are rested along the cylindrical surface of the anode means, so that the anode and guide means can be inserted as a unit into the cathode tube means.

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JOHN H. MACK, *Primary Examiner.*

D. R. JORDAN, *Assistant Examiner.*