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(12) # EUROPEAN PATENT SPECIFICATION

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(54) **Membrane support assembly for electrolytic cell and method of making same.**

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Description

The invention relates to an electrolytic cell comprising a cathode spaced from an anode by a membrane, as well as to a method of making same.

Diaphragm electrolytic cells have been used widely in the production of chlorine and caustic from brine. It is conventional in such cells to employ elongated, hollow finger-shaped cathodes with graphite anodes interdigited between the cathodes. The asbestos diaphragm is customarily deposited in situ on the cathode so as to divide the interior of the cell into a catholyte and an anolyte compartment. Among recent developments have been new, long lasting metal anodes, along with preformed membranes made of polymeric materials which may be either semipermeable (allow only ions to permeate them) or hydraulically-permeable (allowing the electrolyte to permeate them). In spite of the increase of life of these preformed membranes, as well as a number of additional advantages, there is still the problem of fitting these membranes between the cathodes and the anodes in the cell to form fluid tight catholyte and anolyte compartments. These membranes much be fitted over either the anodes or the cathodes and do not naturally adhere to the electrodes as do the asbestos diaphragms which have, for the most part, been formed in situ on one electrode or the other.

As would be expected, those skilled in the art have sought an answer to this particular problem. U.S. patent No. 3,980,544 discloses complex clamping means, requiring major modifications in the electrolytic cells now in use. Any deviation of any of the metal clamp parts disclosed in this patent presents a possibility for a leak. US patent No. 3,878,082 discloses and claims resilient means for holding the diaphragm in place, but does not detail how the edges of the diaphgram or membrane sheet in the region where they separate the catholyte and anolyte compartments are to be sealed. US patent No. 3,923,630 discloses a cylindrical, continuous sheet of preformed membrane positioned about a cylindrical electrode and held in place by being glued or sealed to upper and lower membrane supports. In actual practice it is extremely difficult to completely seal the entire edge of these membrane sheets for the fifty or more electrodes included in each electrode section, and this task is multiplied many times when one considers that a large plant for producing chlorine and caustic may have several thousand electrodes.

The present invention comprises a solution to the above problems and resides in an electrolytic cell comprising a cathode spaced from an anode by a membrane, the improvement comprising a first membrane support plate cast in situ to embed an edge of said membrane and a second membrane support plate cast in situ to embed at least the opposite edge of said preformed membrane in the region where it constitutes the separation between the catholyte and anolyte compartments.

For manufacturing an electrolytic cell of the subject kind the present invention provides a method for supporting a preformed membrane in an electrolytic cell, the improvement comprising the step of casting in situ support plates about the edges of the membrane in the region where they constitute the separation between the catholyte and anolyte compartments.

The advantages of the invention over the prior art are the simple, secure and fluid-tight mounting of the preformed membrane which is economical to produce and radially adaptable to electrolytic cells currently in general industrial use.

The present invention is more clearly illustrated in the accompanying drawings, wherein

Fig. 1 is a perspective view of an electrolytic cell partially in section and shown in a partially assembled state,

Figure 2 is an enlarged, cross-sectional view taken on line II—II of Figure 1,

Figure 3 is an enlarged, cross-sectional view taken on line III—III of Figure 1 and at right angles to Figure 2, and

Figure 4 is a cross-sectional view taken on line IV—IV of Figure 1.

In practicing the present invention, a conventional cell frame 10 is constructed with an inner raised member 11 extending around the entire inner perimeter of the cell frame. The raised member 11 is so formed as to provide ledges 12 which likewise extend around the interior of the perimeter of the cell frame on either side of the raised member 11. The raised member 11 may be an integral part of the cell frame 10, and is so shown in the accompanying drawings. The cell frame itself may be composed of cement, a poured plastic such as polymeric resins, mixtures of polymeric resins with various types of fillers, or any material which is sufficiently strong, relatively non-electrically conducting and nonreactive with the cell environment.

In the embodiment shown in the drawings, an elongated footing strip 14 (see Figure 2) of polymeric resin having raised slots 15 molded therein is glued to the raised member 11 along the bottom 16 of the cell frame. Slots 15 are aligned with openings 18 in the cell frame so as to permit electrolyte to flow in through the bottom 16 of the cell frame and through the anolyte compartment 39. Chlorine passes out of the anolyte compartment 39 through slots 15 in the top 19 of the cell frame, as hereinafter described. An identical footing strip 14 with identical slots 15 is glued to the top 19 of the cell frame. Here the slots 15 are also aligned with openings 18 in the top of the cell frame and provide vents for the chlorine formed in the anolyte compartment of the cell.

A series of hollow finger-shaped cathodes 20, made of wire mesh, are bolted to a steel cathode backboard 21. Cathodes 20 are spaced from one another but in parallel alignment with each other.

Outlets 17 are provided in the backboard 21 for hydrogen and for cell effluent from the catholyte compartment (hereinafter fully defined). The cathode backboard 21, with the cathodes attached, is laid on its back and continuous elongated preformed membrane sheet 22 is laid over the cathodes 20 in a serpentine shape, as best seen in Figure 4. This preformed membrane sheet performs broadly the function generally ascribed to a "diaphragm" in the electrolytic cell. It may be composed of an inert, flexible material which is fluid permeable or one which permits only the passage therethrough of ions (referred to in the art as semipermeable membranes). Such membranes are well known in the art and may be composed of any one of many polymeric, synthetic resins. A preferred composite membrane comprises a perfluorosulfonic acid resin supported by a polyfluoroolefin fabric, and is sold commercially by E. I. duPont de Nemours and Company under its trademark "Nafion".

The preformed membrane sheet 22 is of sufficient width to overhang along its serpentine edges 28 both top and bottom ends 24 of the cathodes 20 (see Figure 2). Elastomeric, foamed pieces (not shown) may be used to hold the serpentine shaped membrane 22 in position, while the entire backboard 21, with cathodes 20 attached, is tipped on end, as shown in Figure 1. This assembly is then moved into the cell frame 10 so that the cathodes are positioned between the raised slots 15 positioned at the top and bottom of the cell frame. The cathode backboard 21 rests in the cell frame on the ledges 12, and is attached to the cell frame 10 by bolts 25 positioned along the perimeter of the backboard.

A molding board (not shown) is seated temporarily in that portion of the ledge 12 which runs along the bottom 16 of the cell frame opposite the cathode backboard 21. A lower membrane support plate 26 is cast in situ by pouring a casting material along the bottom footing strip 14 (note Figure 2). Sufficient casting material is poured along the footing to embed the serpentine edges 28 of the membrane sheet 22 in the casting material. The tops of slots 15, however, should not be covered, since this would prevent the introduction of the brine into the cell. Also, in the embodiment shown, the ends of the cathodes 20 were not embedded in the support plate 26. The lower membrane support plate 26 should be cast in a single pour. If the pour is stopped after the level of the casting material reaches bottom 29 of the serpentine edges 28 of the membrane sheet 22, the already hardened material would prevent the casting material of the second pour from filling in on the backside 27 of the membrane sheet to further embed the serpentine edges 28 (see Figure 2).

An inorganic or organic cementitious material, a polymeric synthetic resin or a material which is the same as or similar to the composition of the cell frame, may be employed as the casting material. This casting material must wet the membrane to form a fluid-tight seal therewith. Furthermore, the casting material should not be attacked by the environment of the electrolytic cell and must be castable at a temperature that does not melt or weaken the membrane sheet. Obviously, the casting material must be sufficiently fluid in the casting state to flow up and around the serpentine edges 28 of the membrane sheet to embed the same in the resulting membrane support plate 26. Vinyl ester resins have been found to be useful as a casting material for the support plates, particularly the reaction product of an unsaturated monocarboxylic acid and a polyepoxide in about equivalent amounts. Fillers, such as sand, may be added to the casting material to provide a heat sink and thus minimize shrinkage upon cooling. After the lower membrane support plate 26 has hardened, the cell frame 10 is reversed so that it rests on the top 19 of the cell frame. At this point an upper membrane support plate (not shown) is cast in exactly the same manner as that heretofore described in connection with the lower membrane support plate 26. The straight (non-serpentine) edges 30 of the membrane sheet 22 which parallel the two sides 31 and 32 of the cell frame, may be sealed in place by laying the cell frame on its back so that it rests on the cathode backboard 21. Casting material 34 is then poured along the interior of the two sides 31 and 32, as shown in Figure 4. In the particular embodiment shown, edges 30 of membrane 22 are wedged between backboard 21 and cell frame sides 31 and 32. Clamps or other types of seals may, of course, be used to provide a fluid-tight seal for the edges 30. The cell is completed by inserting in the cell frame 10 a plurality of anodes 35 held in parallel alignment with one another by means of an anode backboard 36, as shown in Figure 4. It will be further apparent from Figure 4 that each of the anodes 35 is interposed or interdigited between each of the cathodes 20.

Again referring to Figure 4, it is seen that the membrane support assembly, consisting of the membrane sheet 22 and the upper (not shown) and the lower membrane support plates 26 divide the interior of the cell into fluid-tight catholyte compartment 38 and an anolyte compartment 39. The trough portion 40 of the membrane sheet is held in place by the embedment of the serpentine edges 28 in the upper and lower membrane support plates, but is otherwise entirely free of mechanical means that could perforate the relatively fragile membrane sheet 22.

It will be apparent from the above detailed description that the present invention provides means for securely holding the serpentine-shaped membrane sheet 22 in a fluid-tight arrangement which is economical to produce and one which can be readily adapted to electrolytic cells for producing chlorine and caustic which are currently in general industrial use. The trough portions 40 of the membrane sheet 22, which run the entire length of the cathodes, are free from clamps of any kind and are merely held at the edges by the cast-in-place membrane support plates. The improved membrane support assembly is so constructed that both the anodes and the cathodes may be removed from the cell frame without disturbing the membrane sheet 22.

Numerous variations in the embodiment of the invention illustrated in the accompanying drawings will be apparent to those skilled in the art. For example, the "continuous" membrane sheet may in fact be made up of a plurality of short membrane sheets spliced to one another either by gluing or heat sealing. The exact construction of the cell frame 10, or the particular shape of the cathodes and anodes employed in the cell form no part of the present invention, and may be varied widely. For example, hollow, expanded mesh anodes may be employed in place of the solid anodes shown, and punched plate cathodes may be employed in place of the wire mesh cathodes shown.

Claims

1. An electrolytic cell (10), comprising a cathode (20) spaced from an anode (35) by a membrane (22), characterized by a first membrane support plate (26) cast in situ to embed an edge (27, 28) of said membrane, and a second membrane support plate (26) cast in situ to embed at least the opposite edge (27, 28) of said preformed membrane (22) in the region where it constitutes the separation between the catholyte (38) and anolyte (39) compartments.

2. An electrolytic cell (10) for the production of chlorine and caustic from aqueous alkali metal chloride solutions comprising a plurality of cathodes (20) spaced from one another and a plurality of anodes (35) interposed between said cathodes (20) and spaced therefrom, a membrane support assembly which comprises a continuous, elongated sheet of preformed membrane (22) positioned in serpentine fashion between the anodes (35) and the cathodes (20) so as to separate all opposing surfaces of anodes (35) and cathodes (20), characterized by a first membrane support plate (26) cast in situ embedding one serpentine-shaped edge (27, 28) of said membrane (22), and a second membrane support plate cast in situ embedding the opposite serpentine-shaped edge of said membrane, said membrane support assembly dividing said electrolytic cell (10) into separate anolyte (39) and catholyte (38) compartments.

3. The cell of claim 2, characterized by means for sealing the non-serpentine edges (30) of the membrane sheet (22) which comprise a sealant cast in situ of embed all of the non-serpentine edges (30) of said membrane sheet (22).

4. The cell of claim 2 or 3, characterized in that said membrane sheet (22) is a composite membrane composed of a perfluorosulfonic acid resin supported by a polyfluoroolefin fabric.

5. The cell of claim 2, characterized in that said membrane supports (26) are composed of a polymeric material that wets said membrane sheet (22) so as to form a liquid impermeable seal with the embedded portion (27, 28).

6. A method for supporting a preformed membrane in an electrolytic cell, characterized by the step of casting in situ support plates (26) about the edges of the membrane, in the region where they constitute the separation between the catholyte (38) and anolyte (39) compartments.

7. Method of manufacturing an electrolytic cell as defined in claim 3, said method being characterized by the steps of positioning said membrane sheet in serpentine shape between said anodes and cathodes so as to separate all opposing surfaces of said anodes and cathodes, casting a first of said membrane support plates about one serpentine-shaped edge of said membrane sheet so as to fixedly embed said edge in said support plate, and casting a second of said membrane support plates about the other serpentine-shaped edge of said membrane so as to fixedly embed said other edge in said support plate, said membrane support assembly thus forming separate anolyte and catholyte compartments within said electrolytic cell.

8. The method of claim 7, characterized in that said membrane sheet is constructed of a polymeric synthetic resin.

9. The method of claim 7, characterized in that said membrane sheet is constructed of a perfluorosulfonic acid resin supported by a polyfluoro-olefin fabric.

10. The method of any one of claims 6 to 9, characterized by casting the edges of said membrane sheet in an inorganic or organic cementitious material or a polymeric synthetic resin.

11. The method of claim 7, characterized by casting in situ a sealant around non-serpentine edges of the membrane to embed at least a portion of such edges in the sealant and to adhere the edges to at least a wall portion of the cell.

12. The method of any of the claims 6—11 characterized in that each of the membrane support plates is cast in a single pour.

Patentansprüche

1. Elektrolysezelle (10) mit einer durch eine Membran (22) von der Anode (35) getrennten Kathode (20), gekennzeichnet durch eine in-situ gegossene erste Membranträgerplatte (26), die eine Kante (27, 28) der Membran einhüllt und eine in-situ gegossene zweite Membranträgerplatte (26), die mindestens die gegenüberliegende Kante (27, 28) der vorgeformten Membran (22) in dem Bereich, der die Trennung zwischen dem Katholytraum (38) und dem Anolytraum (39) bewirkt, einschließt.

2. Elektrolysezelle (10) zur Herstellung von Chlor und Alkali aus wässerigen Alkalichloridlösungen mit einer Vielzahl von in Abstand voneinander angeordneten Kathoden (20) und einer Vielzahl von zwischen den Kathoden (20) in Abstand davon angeordneten Anoden (35), einer Membranträgeranordnung, die eine endlose ver-

längerte Bahn einer vorgeformten Membran (22) aufweist, die in Schlangenlinie zwischen den Anoden (35) und den Kathoden (20) angeordnet ist, um die einander gegenüberliegenden Oberflächen von Anoden (35) und Kathoden (20) voneinander zu trennen, gekennzeichnet durch eine in-situ gegossene erste Membranträgerplatte (26), die eine der schlangenlinienförmigen Kanten (27, 28) der Membran (22) einhüllt und eine in-situ gegossene zweite Membranträgerplatte (26), die die gegenüberliegende schlangenlinienförmige Kante der Membran einhüllt, wobei die Membranträgeranordnung die Elektrolysezelle (10) in Anolytraum (39) und Katholytraum (38) trennt.

3. Zelle nach Anspruch 2, gekennzeichnet durch Mittel zum Versiegeln der nicht-schlangenlinienförmigen Kanten (30) der Membran (22), die eine in-situ gegossene Siegelmasse, die alle nicht-schlangenlinienförmigen Kanten (30) der Membran einhüllt, sind.

4. Zelle nach Ansprüchen 2 oder 3, dadurch gekennzeichnet, daß die Membran (22) eine Verbundmembran aus von einem Polyfluorolefingewebe getragenen Perfluorsulfonsäureharz ist.

5. Zelle nach Anspruch 2, dadurch gekennzeichnet, daß die Membranträger (26) aus einem Polymermaterial sind, das die Membran (22) benetzt und eine für Flüssigkeit undurchlässige Siegelnaht mit den eingebetteten Membrankanten (27, 28) bildet.

6. Verfahren zum Einbauen einer vorgeformten Membrane in eine Elektrolysezelle, gekennzeichnet durch in-situ-Gießen der Trägerplatten (26) um die Kanten der Membran in dem Bereich, in dem sie eine Trennung des Katholytraumes (38) vom Anolytraum (39) bewirken.

7. Verfahren zum Herstellen einer Elektrolysezelle nach Anspruch 3, das gekennzeichnet ist durch die Schritte Anordnen der Membran in Schlangenlinie zwischen den Anoden und Kathoden, so daß die einander gegenüberliegenden Oberflächen der Anoden und Kathoden voneinander getrennt sind, Gießen der ersten Membranträgerplatte an einer schlangenlinienförmigen Kante der Membran, um die Kante fest in die Trägerplatte einzubetten, Gießen der zweiten Membranträgerplatte, um die andere schlangenlinienförmige Kante der Membran fest in die Trägerplatte einzubetten, so daß die Membranträgeranordnung voneinander getrennte Anolyt- und Katholyträume in der Zelle ausbildet.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Membran aus einem synthetischen Polymerharz ist.

9. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Membran ein von einem Polyfluorolefingewebe getragenes Perfluorsulfonsäureharz ist.

10. Verfahren nach jedem der Ansprüche 6 bis 9, gekennzeichnet durch Eingießen der Kanten der Membran in anorganisches oder organisches Bindemittel oder ein synthetisches Polymerharz.

11. Verfahren nach Anspruch 7, gekennzeichnet durch in-situ-Gießen einer Siegelmasse im die nicht-schlangenlinienförmigen Kanten der Membran, um mindestens einen Tiel dieser Kanten in die Siegelmasse einzubetten und die Kanten mitmindestens einem Teil der Zellwand zu verbinden.

12. Verfahren nach jedem der Ansprüche 6 bis 11, dadurch gekennzeichnet, daß jede der Membranträgerplatten einzeln gegossen wird.

Revendications

1. Cellule électrolytique (10) comprenant une cathode (20) espacée d'une anode (35) par une membrane (22), caractérisée par une première plaque de support de membrane (26) coulée in-situ pour noyer un bord (27, 28) de ladite membrane, et une seconde plaque de support de membrane (26) coulée in-situ pour noyer au moins le bord opposé (27, 28) de ladite membrane préformée (22) dans la région où il constitue la séparation entre les compartiments de catholyte (38) et d'anolyte (39).

2. Cellule électrolytique (10) pour la production de chlore et de caustique à partir de solutions aqueuses de chlorure de métal alcalin comprenant une pluralité de cathodes (20) espacées les unes des autres et une pluralité d'anodes (35) intercalées entre lesdites cathodes (20) et espacées de celles-ci, un dispositif de support de membrane qui comprend une feuille allongée continue de membrane préformée (22) positionnée sous forme d'un serpentin entre les anodes (35) et les cathodes (20) de façon à séparer toutes les surfaces opposées des anodes (35) et des cathodes (20), caractérisée par une première plaque de support de membrane (26) coulée in-situ en noyant un bord en forme de serpentin (27, 28) de ladite membrane (22), et une seconde plaque de support de membrane coulée in-situ en noyant le bord opposé en forme de serpentin de ladite membrane, ledit dispositif de support de membrane divisant ladite cellule électrolytique (10) en compartiments d'anolyte (39) et de catholyte (38) séparés.

3. Cellule selon la revendication 2, caractérisé par des moyens pour fixer hermétiquement les bords non en forme de serpentin (30) de la feuille de membrane (22) qui comprennent une coulée d'un agent d'étanchéité in-situ pour noyer tous les bords non en forme de serpentin (30) de ladite feuille de membrane (22).

4. Cellule selon la revendication 2 ou 3, caractérisée par le fait que la feuille de membrane (22) est une membrane composite composée d'une résine d'acide perfluorosulfonique portée par un tissu de polyfluorooléfine.

5. Cellule selon la revendication 2, caractérisée par le fait que les supports de membrane (26) sont composés d'un matériau polymère qui mouille la feuille de membrane (22) de façon à former un joint étanche imperméable aux liquides avec la partie noyée (27, 28).

6. Procédé pour fixer une membrane préformée dans une cellule électrolytique, caractérisé par l'étape consistant à couler in-situ des plaques de support (26) autour des bords de la membrane, dans la région où ils constituent la séparation entre les compartiments de catholyte (38) et d'anolyte (39).

7. Procédé de fabrication d'une cellule électrolytique telle que définie à la revendication 3, ledit procédé étant caractérisé par les étapes consistant à disposer la feuille de membrane en forme de serpentin entre les anodes et les cathodes de façon à séparer toutes les surfaces opposées dites anodes et cathodes, à couler une première desdites plaques de support de membrane autour d'un bord en forme de serpentin de ladite feuille de membrane, de façon à noyer de façon rigide ledit bord dans ladite plaque de support, et à couler une seconde desdites plaques de support de membrane autour de l'autre bord en forme de serpentin de ladite membrane, pour noyer de façon rigide ledit autre bord dans ladite plaque de support, ledit dispositif de support de membrane formant ainsi des compartiments d'anolyte et de catholyte séparés à l'intérieur de ladite cellule électrolytique.

8. Procédé selon la revendication 7, caractérisé par le fait que la feuille de membrane est constituée d'une résine synthétique polymère.

9. Procédé selon la revendication 7, caractérisé par le fait que ladite feuille de membrane est constitutée d'une résine d'acide perfluorosulfonique portée par un tissu de polyfluorooléfine.

10. Procédé selon l'une des revendications 6 à 9, caractérisé par le coulage des bords de la feuille de membrane dans un matériau de type ciment inorganique ou organique ou une résine synthétique polymère.

11. Procédé selon la revendication 7, caractérisé par le coulage in-situ d'un agent d'étanchéité autour des bords non en forme de serpentin de la membrane pour noyer au moins une partie de ces bords dans l'agent d'étanchéité et pour faire adhérer les bords à au moins une partie de paroi de la cellule.

12. Procédé selon l'une des revendications 6—11, caractérisé par le fait que chacune des plaques de support de membrane est coulée en une seule opération.

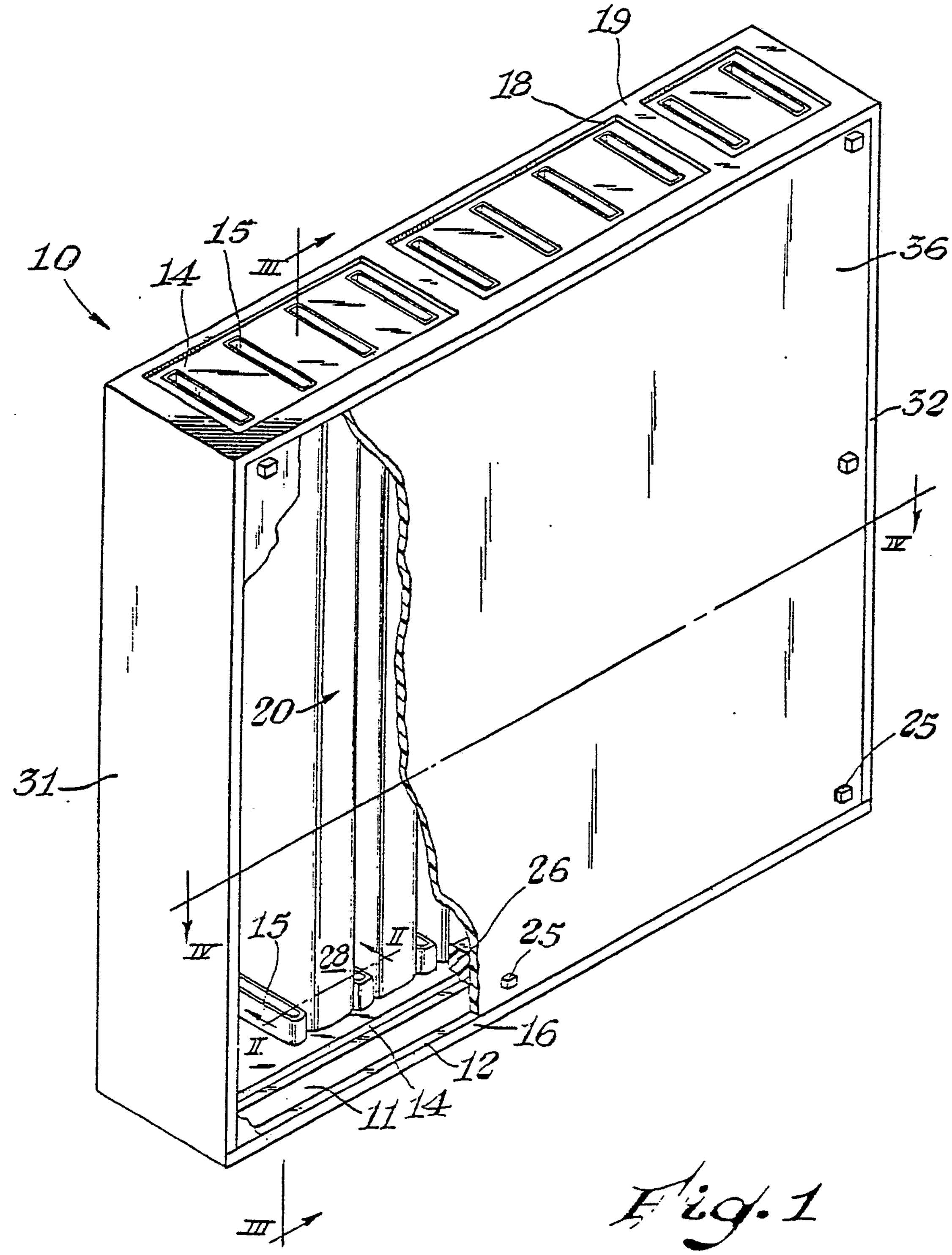

Fig. 1

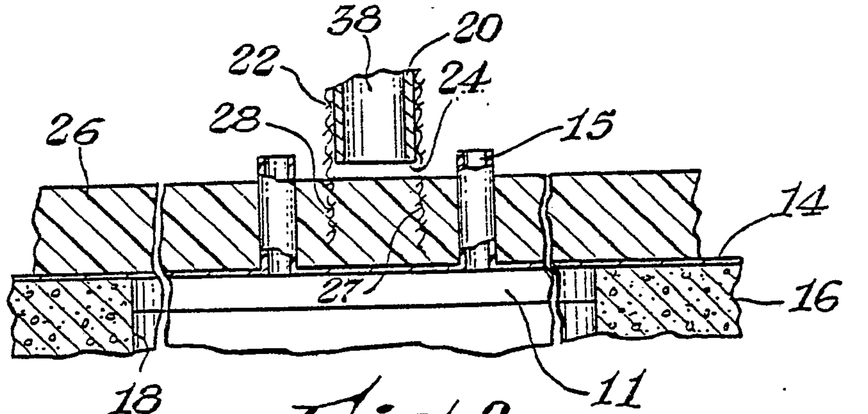

Fig. 2

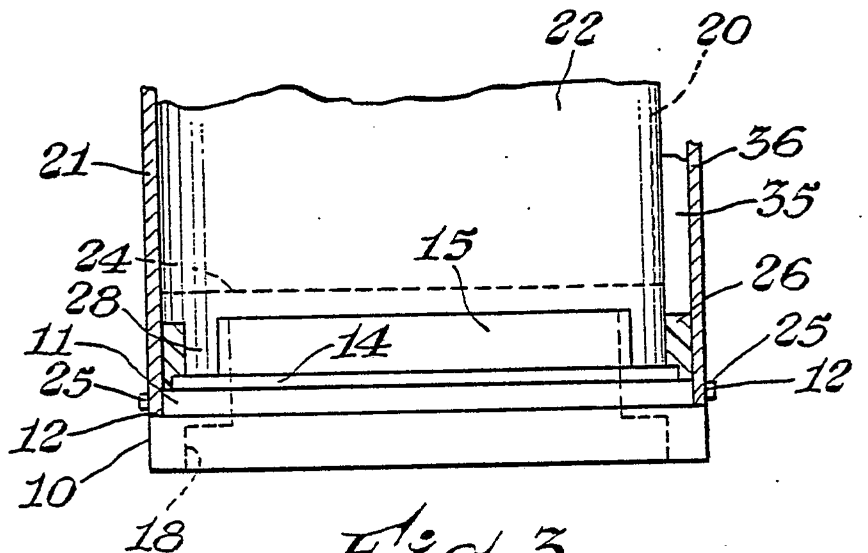

Fig. 3

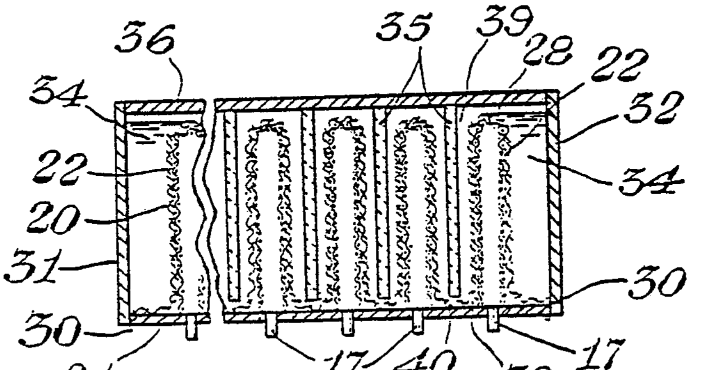

Fig. 4