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(71) Applicant *(for all designated States except US)*: **UHDE-NORA S.p.A.** [IT/IT]; Via Bistolfi 35, I-20134 Milan (IT).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **FEDERICO, Fulvio** [IT/IT]; Via Scalabrini 4, I-29100 Piacenza (IT). **WOLTERING, Peter** [DE/DE]; Sandweg 18, 48485 Neuenkirchen (DE). **CARRETTIN, Leonello** [IT/IT]; Via Soderini 55, I-20146 Milan (IT). **OLDANI, Dario** [IT/IT]; Via Paolo Sarpi 44, I-20154 Milan (IT).

(74) Agent: **PATENTANWÄLTE REITSTÖTTER KINZEBACH**; Sternwartstr. 4, 81679 Munich (DE).

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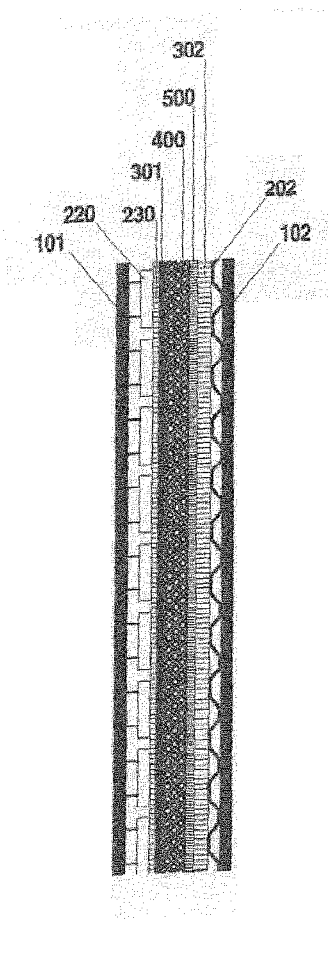
(54) Title: ELASTIC CURRENT DISTRIBUTOR FOR PERCOLATING CELLS



(57) Abstract: It is described a membrane electrolysis cell comprising an anodic compartment and a cathodic compartment, wherein at least one of the two compartments contains a gas- diffusion electrode, and a planar porous element traversed by an electrolyte flow is interposed between membrane and gas-diffusion electrode. The electric current transmission to the gas-diffusion electrode is effected through a current distributor provided with elastic conductive protrusions pushing the electrode against the porous element.

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ELASTIC CURRENT DISTRIBUTOR FOR PERCOLATING CELLS.

DESCRIPTION OF THE INVENTION

The invention relates to a cell for industrial electrolytic processes, and in particular to a cell comprising an anodic compartment and a cathodic compartment separated by an ion-exchange membrane, wherein one or both compartments are equipped with gas-diffusion electrodes and the process electrolyte flows across a percolator or equivalent porous element.

In the following description, reference will be made to a cell suitable for depolarised chlor-alkali electrolysis, that is to the process of alkali chloride brine electrolysis wherein the hydrogen evolution cathodic reaction is inhibited in favour of the reaction of oxygen consumption on a gas-diffusion cathode, for instance as disclosed in EP 1033419; the invention is nevertheless not limited to chlor-alkali cells, being applicable to any industrial electrochemical process making use of gas-diffusion electrodes.

There are known in the art depolarised chlor-alkali cells of particularly advanced type wherein the process electrolyte flows across a suitable porous planar element or percolator under the action of gravity: a cell of such kind is for instance disclosed in WO/0157290. In this kind of cell, there are typically present an anodic compartment obtained from a titanium shell, fed with an alkali chloride concentrated brine and containing a titanium anode provided with a catalytic coating for chlorine evolution, and a cathodic compartment delimited by a nickel cathodic shell; the two compartments are separated by a cation-exchange membrane. The caustic soda produced in the process flows by gravity across a porous element inserted in the cathodic compartment contacting on one side the ion-exchange membrane, on the other side a gas-diffusion cathode. In other words, while the anode is a stiff metallic element which is electrically and mechanically connected to the anodic shell by means of a suitable metal structure selected among those known in the art, for instance an array of ribs, the cathode is a thin porous element obtained from a silver net, a carbon cloth or other type of non self-standing equivalent structure. For this reason, the current transmission from the back-wall of the cathodic shell to the gas-diffusion electrode must be effected by means of a structure providing a more delocalised contact and capable of mechanically supporting the electrode. In order to improve the electrochemical features, it is also necessary that the cathode be pushed against the percolator with a certain pressure, indicatively 0.1 to 0.5 kg/cm², so as to allow the electrical continuity while contributing to the confinement of the circulating liquid electrolyte. To satisfy all of the above conditions, the cells of the prior art are provided with an electric current feed system relying on two distinct elements: firstly, a rigid current collector integral to the cathodic shell which may for instance consist of a rib array, as in the anodic side; secondly, a metal mattress positioned between the rigid current collector and the gas-diffusion electrode, which is capable, in conditions of suitable compression, to transmit a sufficient pressure to the gas-diffusion electrode thereby ensuring the required electrical continuity. An equivalent solution is applied for the retrofitting of chlor-alkali cells of the traditional type, to adapt the same to a percolation-type depolarised process, for instance as illustrated in figure 2 of WO 03/102271: in this case, the original cell cathode, which is a metallic electrode for hydrogen evolution made of nickel or steel, as known in the art, takes the role of the current collector, while a nickel mattress (elastic current collector) acts as the intermediate element for current transmission between the rigid current collector and the gas-diffusion electrode.

The above indicated solution entails however a few inconveniences hampering the commercialisation of this type of cells: the two-component type current transmission system involves in fact excessive costs and thicknesses, difficulties of installation and of dimensional control of the mattress (especially in the peripheral zone), difficulty of controlling the deformations and the elastic forces, besides of course adding a contact interface not particularly favourable in terms of ohmic drop, such as the one between mattress and gas-diffusion electrode.

It is one object of the present invention to provide an electrolytic cell separated by an ion-exchange membrane and equipped with gas-diffusion electrode and percolator element for electrolyte circulation overcoming the limitations of the prior art.

Under another aspect, it is one object of the present invention to provide an improved electric current feed system for an electrolytic cell provided with gas-diffusion electrode and percolator.

The invention consists of an electrolysis cell with an anodic compartment and a cathodic compartment separated by an ion-exchange membrane, wherein at least one of the two compartments is equipped with a gas-diffusion electrode having two major surfaces, a first major surface facing the membrane being in contact with a percolator traversed by an electrolyte flow, and a second major surface, opposed to the first major surface, being in contact with a current distributor comprising a multiplicity of elastic conductive protrusions suitable for compressing the gas-diffusion electrode against the percolator. As percolator it is intended any porous planar element suitable for being traversed by gravity by a liquid flow, as disclosed in WO/0157290. In one preferred embodiment, the current distributor, which replaces the rigid current collector-elastic current collector assembly of the prior art, is obtained by cutting and shaping of a single metal sheet, for instance a nickel sheet in the case of a cathodic collector for chlor-alkali cells. In this case, the nickel sheet is a sheet of thickness typically comprised between 0.5 and 1.5 mm, preferably provided with a coating suitable for reducing the contact resistance. The nickel material of the sheet may be variously alloyed and for instance selected from the assortment of commonly available products; the choice of a nickel material of grade and mechanical characteristics suitable for the manufacturing of springs, for instance with superior elastic features, will prove particularly advantageous. In one particularly simple and effective embodiment, the conductive protrusions capable of imparting a sufficient pressure to the electrode are spring tags arranged in couples so that two adjacent spring tags protrude in opposite direction from the major plane of the metal sheet from which they are obtained. In this way a more effective and homogeneous support of the whole electrode surface is obtained. The above indicated solution is suited to an optimum cell design in almost every process condition; nevertheless, the use of the mattress according to the prior art as a contact element at high current density has the advantage of allowing an effective gas circulation (for the case of depolarised chlor-alkali electrolysis for example, an effective supply of oxygen to the gas-diffusion electrode) which could fall short with a simple lamellar structure. In this case, a particularly preferred embodiment provides the conductive protrusions to be in form of individual tiles, in their turn comprising one or more spring tags for providing the electrical contact but also one or more openings to favour the gas passage. The conductive protrusions may for instance be disposed in parallel rows distributed along the whole electrode surface.

The current distributor in accordance with the invention is suitable for achieving an efficient electrical contact directly on the gas-diffusion electrode surface, at a pressure preferably comprised between 0.1 and 0.5 kg/cm², thereby getting rid of a contact interface with respect to the system of the prior art in which a rigid current collector is coupled to an elastic current collector; on the other hand, in one embodiment of the invention an additional element for distributing the mechanical compression force may be inserted between current distributor and gas-diffusion electrode, for example consisting of a thin mesh, or of an expanded or punched sheet. In such case the number of contact interfaces is equivalent to that of the prior art, nevertheless the corresponding resistance is substantially lower than what would be obtained with the scarcely elastic mattress of the prior art directly in contact with a gas-diffusion electrode. Moreover, as it will be easily appreciated by one skilled in the art, the overall thickness of the cell is substantially lower.

The invention will be described more in detail with the aid of the attached drawings, which have a merely exemplifying purpose and are not intended to limit the invention.

- Figure 1 represents a percolation type depolarised chlor-alkali cell according to the prior art.
- Figure 2 represents a percolation type depolarised chlor-alkali cell according to the present invention.
- Figure 3 represents a first embodiment of the current distributor according to the invention.
- Figure 4 represents a second embodiment of the current distributor according to the invention.
- Figure 5 represents a third embodiment of the current distributor according to the invention.

In figure 1 it is shown a percolation type depolarised chlor-alkali cell according to the prior art, comprising one anodic and one cathodic compartment separated by an ion-exchange membrane (500). The cathodic compartment is delimited by a cathodic back-wall (101), in contact with an electric current feed system relying on two distinct elements, a rigid current collector (201) integral thereto, and an elastic current collector (210) consisting of a mattress, for instance made of nickel. The cathode (301) consists of a porous gas-diffusion electrode fed with oxygen, contacting on one side the mattress (210), on the other side a percolator (400) consisting of a planar porous element traversed by the electrolyte flow under the action of gravity. The ion-exchange membrane (500) acting as the separator has a cathodic surface in contact with the percolator (400) and an anodic surface facing an anode (302) which may be in contact therewith or kept at a small predetermined distance. The anode (302) is normally comprised of a titanium substrate consisting of a mesh or of an expanded or punched sheet, or optionally of a juxtaposition of two such elements; the anodic substrate is provided with a catalytic coating for chlorine evolution as known in the art. The electrical continuity between anode (302) and anodic compartment back-wall (102) is ensured by a rigid current collector (202). The cathodic (201) and anodic (202) rigid current collectors may consist of rib arrays, undulated sheets, sheets provided with suitably spaced gophers or other types of current collectors as known by those skilled in the art.

In figure 2 it is shown a percolation type depolarised chlor-alkali according to the present invention, wherein the elements in common with the cell of figure 1 are indicated by the same reference numerals.

The electric current feed system consists of a multiplicity of conductive protrusions (220), for instance an assembly of springs or elastic spring tags suitable for compressing the gas-diffusion electrode (301) against the percolator (400); between the assembly of conductive protrusions (220) and the gas-diffusion electrode (301) an optional element for distributing the mechanical compression force (230) is inserted, for instance a thin mesh, or an expanded or punched sheet.

Figure 3 shows one embodiment of the multiplicity of conductive protrusions obtained from a single metal sheet and consisting in this case of an assembly of elastic spring tags (221) disposed in parallel according to a comb-like geometry: the spring tags are arranged in couples, so that each two spring tags protrude in opposite directions from the major plane of the original metal sheet. Depending on the cell size, a single row of spring tags (221) may cover the whole active surface, or more rows may be arranged side by side, as will be evident to one skilled in the art.

Figure 4 shows a preferred embodiment of the multiplicity of conductive protrusions obtained from a single metal sheet: in this case the protrusions are preferably quadrangular individual tiles (222) obtained by cutting and shaping of a sheet, optionally welded directly to the rigid current collector (201), each of them comprising elements performing different functions: for example, by means of a suitable folding step, each tile is provided with edges with a curvature angle of about 90° (223) in order to impart the required stiffness. A multiplicity of suitably spaced apart spring tags (224) acts as the contact element with the gas-diffusion electrode (301), and a multiplicity of holes (225) favours the gas supply and circulation, in this case with particular reference to the oxygen required for the cathodic reaction. The various tiles welded to the rigid current collector (201) are preferably arranged on optionally off-set parallel rows.

Figure 5 shows a variation of the preferred embodiment shown in figure 4 of the multiplicity of conductive protrusions obtained from a single metal sheet: in this case the original metal sheet is a punched sheet, and the multiplicity of holes (225') extends on the whole body of the tile (222), including the spring tags (224). In this way an enhanced gas supply is obtained, also effective when the spring tags (224) are compressed until the end of stroke, coming in contact with the sheet from whence they are projected. An albeit marginal saving in the manufacturing phase is also obtained, consisting of the independent execution of holes (225) indicated on tile (222) of figure 4. The tile configuration also presents a further mechanical advantage: in case of a sudden high cathode counterpressure (for instance due to errors in the control of process conditions, or to element handling and assembling mistakes), the spring tags do not undergo a permanent deformation in view of the abutment of the GDE on the whole tile surface. In this case, the fact that the tiles are obtained from a punched sheet is even more important to guarantee the correct gas supply in any case, as is it evident to one skilled in the art.

EXAMPLE 1

A lab experimental electrolysis cell of 0.16 m^2 active area was equipped according to the scheme of figure 2 with a titanium DSA® anode (302) provided with a ruthenium and titanium oxide-based catalytic coating, a Nafion® N982 ion-exchange membrane (500) commercialised by Dupont/USA, a nickel foam percolator, a gas-diffusion electrode consisting of a silver net activated with a silver-based catalyst.

The electric current feed system was comprised of a multiplicity of elastic conductive protrusions each consisting of a tile (222) as illustrated in figure 5, obtained from a 1 mm thick nickel punched sheet.

The cell anodic compartment was fed with a circulating sodium chloride brine having a concentration of 210 g/l, at a current density of 4 kA/m² and at a temperature of 90°C. The cathodic product consisted of 32% by weight caustic soda flowing downwards across the percolator. In these conditions, after stabilising the process conditions on the plant for ten days, a cell voltage comprised between 2.00 and 2.05 V was detected.

EXAMPLE 2

The test of example 1 was repeated in analogous conditions, making use of a cell of the prior art. The only substantial difference consisted therefore in the cathodic current feed system, comprising a rigid current collector structure consisting of a nickel rib array welded to the cathodic back-wall coupled to a commercial nickel mattress.

In the same process conditions of example 1, after ten days of stabilisation a cell voltage comprised between 2.10 and 2.15 V was detected.

The foregoing description is not intended to limit the invention, which may be used according to different embodiments without departing from the scopes thereof, and whose extent is univocally defined by the appended claims.

Throughout the description and claims of the present application, the term "comprise" and variations thereof such as "comprising" and "comprises" are not intended to exclude the presence of other elements or additives.

CLAIMS

1. Electrolysis cell of the type comprising an anodic compartment and a cathodic compartment separated by an ion-exchange membrane, at least one of said compartments equipped with a gas-diffusion electrode having two major surfaces, the first major surface of said gas-diffusion electrode facing the membrane and being in contact with a planar porous element suitable to be traversed by an electrolyte flow, the second major surface of said gas-diffusion electrode being in contact with a current distributor comprising a multiplicity of elastic conductive protrusions suitable for compressing said gas-diffusion electrode against said planar porous element.
2. The cell of claim 1 wherein said multiplicity of conductive protrusions exerts a pressure of 0.1 to 0.5 kg/cm^2 on the gas-diffusion electrode.
3. The cell of claim 1 or 2 wherein said current distributor comprising said multiplicity of conductive protrusions is obtained by cutting and shaping of a metal sheet.
4. The cell of claim 3 wherein said conductive protrusions are spring tags arranged according to a comb-like geometry.
5. The cell of claim 4 wherein said spring tags are arranged in adjacent pairs and the spring tags of each of said pairs protrude in opposite directions from the major plane of said metal sheet.
6. The cell of claim 3 wherein said conductive protrusions are optionally quadrangular individual tiles comprising a multiplicity of spring tags and at least one opening for gas circulation.
7. The cell of claim 6 wherein said tiles are welded to a rigid current collector in optionally off-set parallel rows.
8. The cell of any one of claims 3 to 7 wherein said metal sheet has a thickness of 0.5 to 1.5 millimetres.
9. The cell of any one of claims 3 a 6 wherein said metal sheet is a punched sheet.
10. The cell of any one of claims 3 a 9 wherein said metal sheet is made of nickel.
11. The cell of claim 10 wherein said nickel sheet is provided with a coating suitable for reducing the electric contact resistance in correspondence of said protrusions.

12. The cell of any one of the previous claims comprising an additional element for distributing the mechanical compression force selected from the group of meshes, punched sheets and expanded sheets inserted between said current distributor and said gas-diffusion electrode.

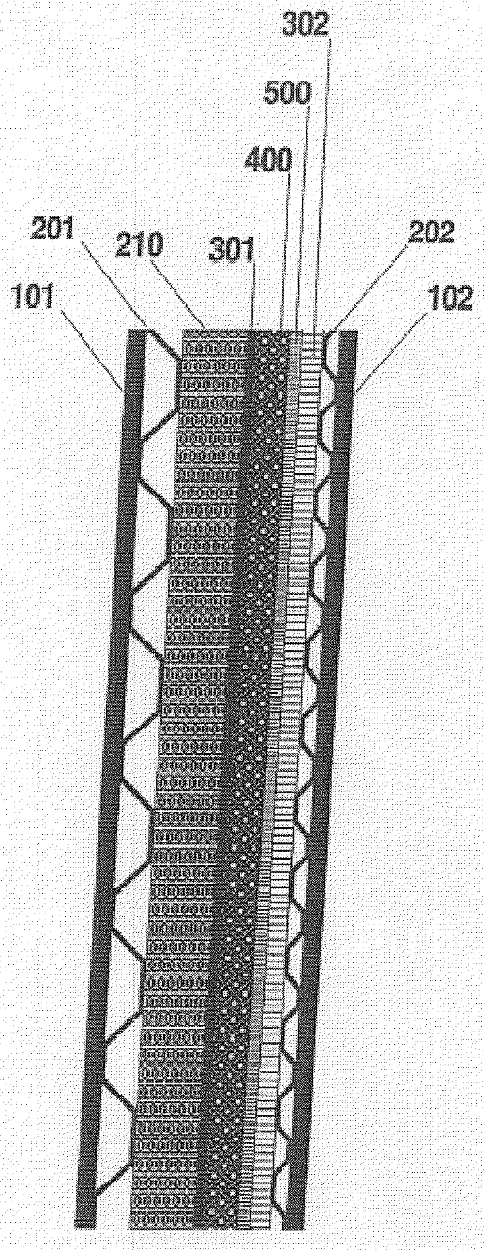

Fig. 1

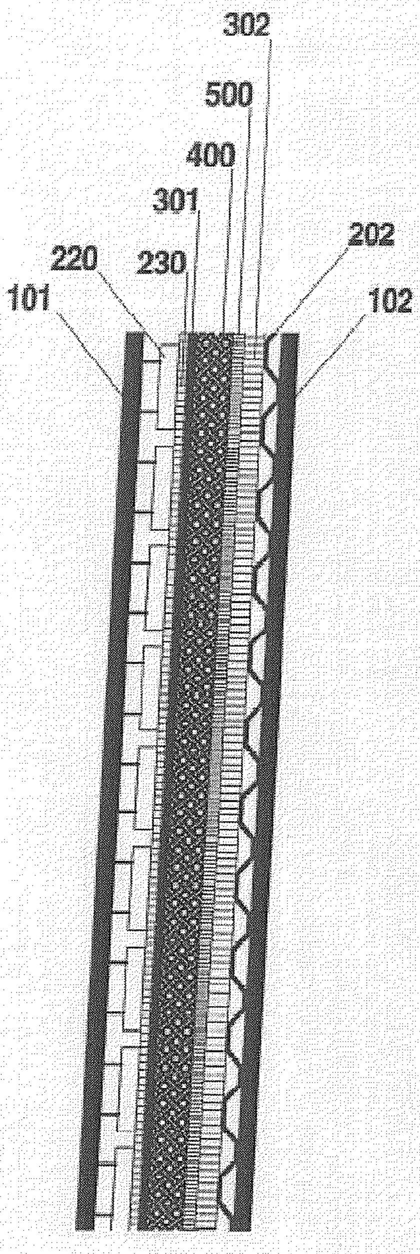

Fig. 2

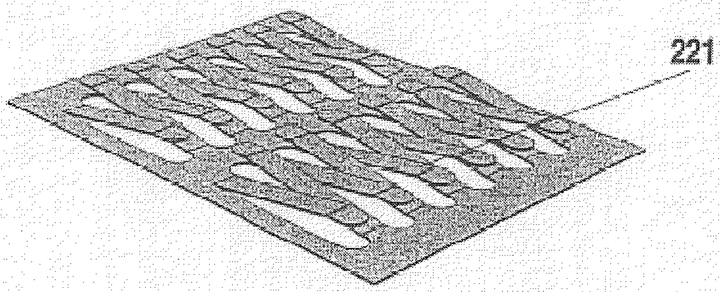

Fig. 3

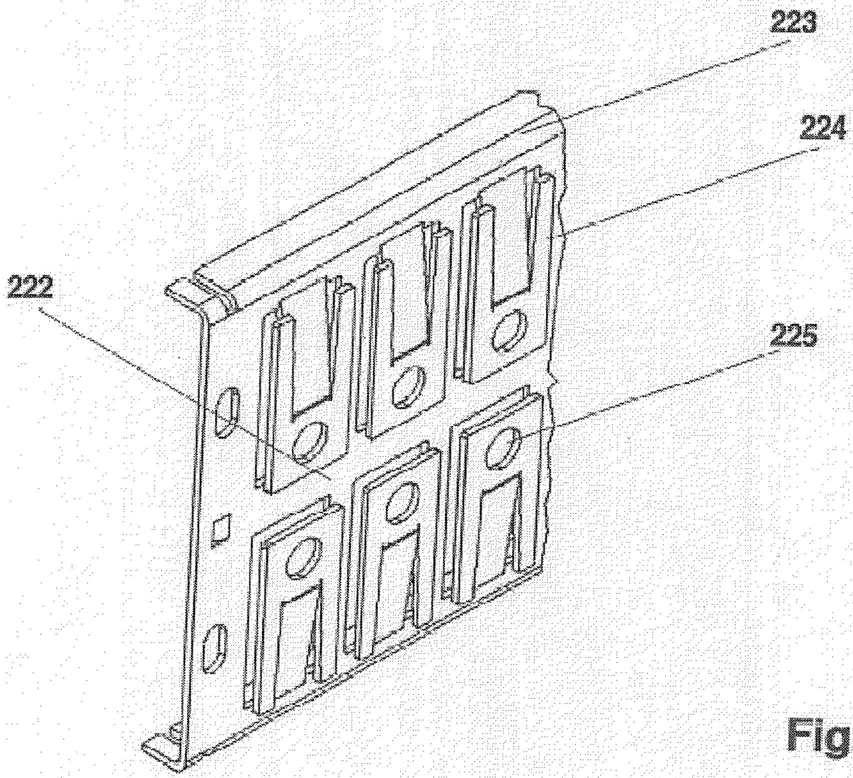

Fig. 4

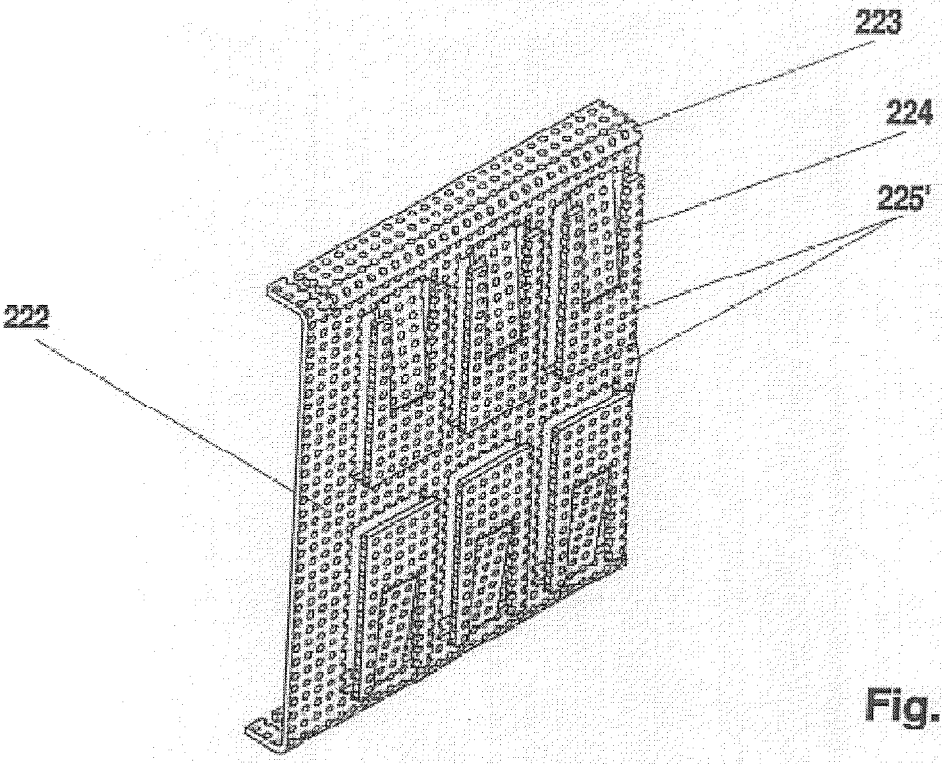

Fig. 5