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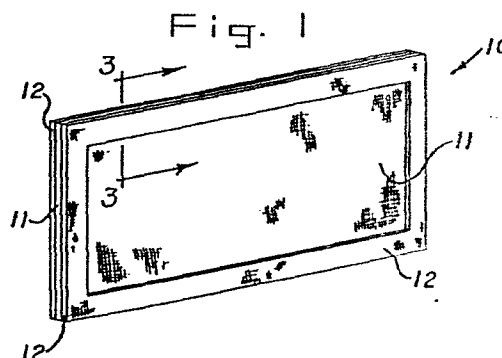
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54 **Membrane unit for electrolytic cell.**

57 A membrane unit for use in an electrolytic cell comprising a combination of a membrane material (11) and a reinforcing material (12) around only the gasket-bearing surface of the membrane material. Damage to the gasket bearing surface of the membrane structure is minimized when the membrane unit is employed in, for example, electrolytic cells of the filter press-type.



MEMBRANE UNIT FOR ELECTROLYTIC CELL

This invention relates to membranes for use in electrolytic cells and, more particularly, to a membrane unit which will resist tearing upon application of a compressive force to a gasket bearing
5 surface of the membrane.

There are many well-known membranes for use in electrolytic cells. For example, typical membranes include the perfluorinated carboxylic or sulfonic cation exchange membranes such as the Nafion® membranes
10 manufactured by E. I. duPont de Nemours and Company or the Flemion® membranes manufactured by Asahi Glass Company, Ltd. These membranes are typically available in sheet form and employed in filter press-type or flat plate-type electrolytic cells having monopolar or
15 bipolar electrodes. Examples of bipolar, filter press-type cells are described in U.S. Patent Nos. 4,111,779 and 4,108,742. These cells are used, for example, to carry out electrolysis of an aqueous alkali metal halide to produce a halogen, for example chlorine,
20 and an alkali metal hydroxide such as sodium hydroxide. Generally, the bipolar, filter press-type electrolytic cell is composed of several bipolar unit cells arranged

in series. One bipolar unit cell has an anode and cathode compartment separated by a partition wall. Typically, the anode and cathode are attached to opposite sides of the partition wall. The membrane is
5 usually interposed between two adjacent unit cells to separate the anode compartment from the cathode compartment. A plurality of anode and cathode frames are installed in a parallel fashion and a longitudinal compressive clamping means is applied to the anode and
10 cathode frames with the membrane interposed between the frames to form the electrolytic cell in toto.

It is common practice to interpose a gasket between the membrane and the anode or cathode frame to provide the electrolytic cell with fluid-tight, i.e., a
15 liquid- and gas-tight seal to prevent leakage of electrolyte between anode and cathode compartments or to the atmosphere. It is important to have a complete liquid- and gas-tight seal in electrolytic cells because these cells typically operate under corrosive
20 environments. Generally, one side of the gasket is in contact with the lateral face of an electrode frame and the other side of the gasket is in contact with one side of the membrane's peripheral surface.

Typical gasket materials include resilient
25 material such as rubber or an elastomer. Commercial bipolar membrane electrolyzers generally use ethylene-propylene (EPM) or ethylene-propylene-diene (EPDM) as gasket material between the membrane and electrode frames. These materials tend to deform and expand
30 outwardly as pressure is applied to the frames via the frame members. As the gaskets deform outwardly, certain membranes which are in contact with the gaskets

tend to stretch when they are pulled under the pressure of the outwardly deforming gaskets. This stretching of the membrane beneath the gaskets employed on adjacent electrode frames can cause the membranes to break or
5 tear when attempting to compress the frames into a fluid-tight cell. In addition, resilient gaskets require a high compressive force to effect a seal which increases the risk of breaking or tearing the membrane.

Any tears or breaks in the membranes may
10 reduce current efficiency during operation, greatly increasing electrical current usage while reducing the electrolytic operating efficiency of the cell. Too great a drop in current efficiency and/or electrolytic operating efficiency can require costly shutdown of the
15 entire cell while the damaged membrane or membranes are replaced.

The present invention is an ion exchange membrane unit comprising at least one layer of a first material adapted for use as an ion exchange membrane
20 and at least one layer of a second material adapted to reinforce the membrane, said reinforcing layer being secured to at least one side of the membrane around a gasket-bearing peripheral surface of the membrane.

The present invention also resides in a
25 method of sealing an electrolytic cell comprising the steps of

(a) interposing at least one gasket between at least one electrode frame and an ion exchange membrane in an electrolytic cell, said membrane comprising at

least one layer of a material adapted for use as an ion
exchange membrane and at least one layer of a material
adapted to reinforce the membrane, said reinforcing
layer being secured to at least one side of the mem-
5 brane around the gasket-bearing peripheral surface of
the membrane; and

(b) applying a compressive force to the cell.

Although alternative embodiments of the
present invention are shown in the following Figures,
10 the same reference numbers are used in the drawings to
describe identical elements.

Figure 1 is a perspective view of the mem-
brane unit of the present invention showing a membrane
sheet having a reinforcement material along the
15 periphery of the sheet.

Figure 2 is a perspective view of another
embodiment of the present invention showing a membrane
having a plurality of openings and a reinforcing mate-
rial along the periphery of the sheet.

20 Figure 3 is a cross-sectional view taken
along line 3-3 of Figure 1.

Figure 4 is a cross-sectional view of an
alternate embodiment of the present invention showing
a membrane having a reinforcement material on one
25 planar peripheral surface of the membrane sheet.

Figure 5 is a cross-sectional view taken
along line 5-5 of Figure 2.

Figure 6 is a sectional view showing a portion of an electrolytic cell series assembly including the membrane unit of Figure 1.

With reference to Figure 1, a rectangular sheet 11 made of a membrane material is shown with a layer of a reinforcing material 12 attached, bonded or otherwise adhered to a peripheral portion of the membrane on opposite planar surfaces thereof. Figure 3 more clearly illustrates the reinforcing material 12 as a strip secured to both sides of the membrane 11 and only along a gasket-bearing surface of the membrane. Figure 4 shows the reinforcing material 12 applied to only one planar surface of the membrane and only along the peripheral, gasket-bearing surface of the membrane. "Gasket-bearing surface" is defined as that portion of the periphery of the membrane sheet which is subject to compression forces in order to effect a seal at the periphery of an electrode frame of an electrolyzer. In Figure 1, the reinforcing material 12 has a picture-frame shape. It is to be understood, however, that the membrane unit or structure of this invention is not limited to a rectangular sheet but can be circular or of some other desired shape.

The membrane 11 is made of a material having ion exchange properties. Such membrane is substantially impervious to the hydrodynamic flow of the electrolyte and the passage of gas products produced during electrolysis. Suitable are cation exchange membranes such as those composed of fluorocarbon polymers having a plurality of pendant sulfonic acid groups or carboxylic acid groups or mixtures of sulfonic and carboxylic acid groups. The terms "sulfonic acid groups" and "carboxylic acid groups" are meant to include salts of

sulfonic acid or salts of carboxylic acid which are suitably converted to or from the acid group by processes such as hydrolysis. An example of a carboxylic acid type cation exchange membrane is commercially
5 available from Asahi Glass Company under the trademark Flemion®. Another example of a suitable membrane having cation exchange properties is a perfluoro-sulfonic acid membrane sold commercially by E. I. duPont de Nemours and Company under the trademark
10 Nafion®.

The reinforcing material 12 can be made of any material suitable for strengthening the gasket bearing surface area of the membrane 11. The reinforcing material 12 can be of the same or different
15 material as the membrane. Preferably the reinforcing material 12 should have a heavier scrim than that of the membrane material. Both the membrane and the reinforcing material should be made of a corrosion-resistant, non-contaminating material which is stable
20 upon contact with electrolyte media present in an electrolytic cell. Suitable materials which can be employed in accordance with this invention include, but are not limited to, the following: fluorine-containing polymers such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene copolymer (FEP) and perfluoroalkoxy resin (PFA); polysulfide polymers, polyvinyl chloride, fluoroelastomers such as Viton®, a trademark of E. I. duPont de Nemours and Company, and chlorosulfonated polyethylenes such as Hypalon®, a
25 trademark of E. I. duPont de Nemours and Company.
30

The reinforcing material 12 can be attached or otherwise secured to the membrane 11 by any well known method in the art, for example, bonding with an

adhesive, heat sealing, or ultrasonic sealing. It is preferred to heat seal the reinforcing material to the membrane.

5 In Figures 2 and 5, the membrane 11 contains perforations or openings 13 along its periphery or gasket-bearing surface. The reinforcing material 12 is secured to the gasket bearing surface and covers the openings 13 on both sides of the membrane 11. The membrane having such openings 13 allows the reinforcing material 12 on one side of the membrane to form a bond through the membrane to the reinforcing material 12 on the opposite side through the openings 13. This is particularly useful when bonding a reinforcing material which is difficult to attach to the membrane material.

10

15 Generally, when the reinforcing material and the membrane material are made of dissimilar materials, opening 13 should be provided in the peripheral surface of the membrane to provide additional securement of the reinforcing material to the membrane.

20 Referring to Figure 6, an electrolysis cell assembly is shown wherein a membrane unit generally designated by reference number 10, comprising a membrane 11 and a reinforcing material 12 attached to both sides of the membrane 11, is interposed between two electrode frame units 14. A gasket 18 may be interposed between the membrane unit 10 and an electrode frame 14. It is also within the scope of the invention to interpose a gasket 18 on both sides of the membrane unit 10 and two adjacent electrode frames 14. Any

25

30 gasket used in an electrolytic cell of the filter press type may be used. The gasket should be made of a corrosion resistant material, should have a high volume

resistivity and good sealability after it has been compressed. Suitable materials for the gasket 14 may be, for example, EPDM, a chlorinated polyethylene (CPE), a polytetrafluoroethylene such as Teflon®,
5 manufactured by E. I. duPont de Nemours and Company, and reinforced asbestos. An anode 15 and a cathode 16 are electrically connected with connectors 17 through the electrode frame 14. The electrolysis assembly
10 above is typical of bipolar electrolytic cells of the filter press type such as described in U.S. Patent Nos. 4,111,779 and 4,108,742. Any cell of the filter press type may be used in the present invention.

In order to effect sealing of the periphery of the electrode frame 14, the membrane unit 10 and a
15 gasket 18 are interposed between two adjacent electrode frames 14 and a compressive force is applied to the cell assembly. The compressive force may be applied by any means known to those skilled in the art, for example, by clamping the frames together or by using a hydraulic
20 ram. Preferably a hydraulic ram is used to squeeze the electrode frames, gaskets and membranes together. The actual compressive force applied will be dictated by the type of material used for the gasket.

The invention will be illustrated further in
25 the examples which follow.

Example 1

A 10 cm by 10 cm test sample of Nafion® 901 membrane, obtained from the duPont Company of Wilmington, Delaware, was reinforced by heat sealing strips of PFA
30 fluoroplastic film around the edges on both sides of the membrane. Any heat-sealing technique known in the art

may be used. In this instance, the heat sealing was performed by the EGC Corporation of Houston, Texas, under contract to The Dow Chemical Company. The film thickness used on the cathode side of the membrane was 15 mils thick while the film thickness used on the anode side of the membrane was 5 mils thick. The actual design used is the design shown in Figures 1 and 3.

A laboratory electrolytic cell was used for testing the test samples. The cell consisted of an anode compartment frame and a cathode compartment frame. The anode compartment frame was made of titanium having the titanium surface located under the gasket area coated with a ruthenium dioxide coating to avoid possible crevice corrosion problems. The cathode compartment frame of the cell was made of an acrylic polymer. The anode of the cell was made of titanium with a ruthenium dioxide coating and the cathode was a nickel cathode.

The gasket used was a 6.35 mm thick gasket made of EPDM rubber purchased from the Prince Rubber & Plastics Co., Inc. of Buffalo, New York. The gaskets were cut from single EPDM rubber sheets to form a picture-frame shape with dimensions of 9.5 cm outside-to-outside and 7.62 cm inside-to-inside. Thus, the width of the gasket surface was 9.5 mm. The total gasket area was 32.65 cm². The gasket was used on both sides of the membrane and contact loading was distributed over the reinforced surface.

Ten 9.5 mm diameter bolts were torqued to 12 ft-lbs (16.3 Joules) force to press together the anode

and cathode compartments, the membrane and gaskets resulting in a total force of 8,626 kg from the bolt loading. The force exerted on the membrane under the gaskets was equivalent to 25,856 kPa. The force used on
5 this test sample was ten times greater than the force used on the test sample described in the Comparative Example A, below.

The cell of this example was operated to produce 32 weight percent caustic while controlling the
10 anolyte salt at 200 grams per liter sodium chloride concentration. The cell temperature was maintained at 90°C with ampere loading controlled at 0.31 amp/cm² of projected anode area current density. The test was conducted for 210 days and during this period the
15 caustic current efficiency averaged 95 percent with an average cell voltage of 3.5. The cell operated without leaks and performed without complications.

Visual inspection of the membrane after dismantling the cell showed the membrane to be in
20 excellent condition with no tears or breaks in the gasket contact and loading area. Thus, the reinforcing concept of the invention protected the membrane from damage and showed a successful improvement over the membrane used in the Comparative Example A, below.

25 Comparative Example A

A 249 cm by 127 cm test sample of Nafion® 324 membrane, obtained from the duPont Company of Wilmington, Delaware was used in this test. The gasket surfaces of the membrane were not reinforced.

The electrolytic cell used in this test is described in U.S. Patent application Serial No. 472,792, filed March 7, 1983, and is of a type well known in the industry as a bipolar flat plate-type cell having a nominal size of 1.22 met. by 3.05 met. The cell contained an anode of titanium with a ruthenium oxide coating and a cathode of steel.

The gasket used was a 4.76 mm thick gasket made of EPDM rubber purchased from the Prince Rubber and Plastics Co., Inc., of Buffalo, New York. Specifications for the EPDM include "EPDM for Chlor-Alkali Service, Prince #6962." The gaskets were cut from single EPDM rubber sheets to form a picture-frame shape with dimensions of 2.47 meter outside-to-outside and 2.37 meter inside-to-inside in the long direction and 1.25 meter outside-to-outside and 1.15 meter inside-to-inside in the short direction. Thus, the width of the gasket surface was 5.1 cm. The total gasket area was 3,676 cm². The gasket was used on both sides of the membrane and contact loading was distributed over the reinforced surface.

A hydraulic cylinder in a filter press arrangement was used to press together the cell units. The total force resulting from the action of the hydraulic press was 78,152 kg. The force exerted on the membrane was equivalent to 2,080 kPa.

The cells were operated to produce from 12 to 16 weight percent caustic while controlling the anolyte salt at 200 grams per liter sodium chloride concentration. The cell temperature was maintained at 90°C with D.C. current controlled at 10.0 kiloamperes.

Thus, the ampere loading was 0.31 amperes per square
cm of projected anode area current density. The test
was conducted for 199 days and during this period, the
caustic current efficiency averaged 82-84 percent which
5 was 4 percent below the expected caustic current efficiency
for Nafion® 324.

Visual inspection of the membrane after dis-
mantling the cell showed the membrane to have severe
damage in the areas beneath the gaskets and in the area
10 next to the gaskets. The gasket loading forces had
stretched and cracked the membrane so severely to
render the overall cell performance unsatisfactory.

1. An ion exchange membrane unit comprising at least one layer of a first material adapted for use as an ion exchange membrane and at least one layer of a second material adapted to reinforce the membrane, said
5 reinforcing layer being secured to at least one side of the membrane around a gasket-bearing peripheral surface of the membrane.

2. The membrane unit of Claim 1 wherein the composition of the reinforcing material is of the same composition as the membrane.

3. The membrane unit of Claim 1 or 2 wherein the membrane material has at least one opening and the reinforcing material is heat sealed to the membrane material through the opening.

4. The membrane unit of Claim 1, 2 or 3 wherein the reinforcing material has a thickness of from 0.076 to 0.51 mm.

5. The membrane unit of any one of the preceding claims wherein the reinforcing material has a heavier scrim than that of the membrane material.

6. The membrane unit of any one of the preceding claims wherein the membrane material is composed of fluorocarbon polymers having a plurality of pendant sulfonic acid groups, carboxylic acid groups or mixtures of sulfonic acid groups and carboxylic acid groups.

7. An electrolytic cell comprising the membrane of Claim 1 separating at least two electrode compartments.

8. A method of sealing an electrolytic cell comprising the steps of

(a) interposing at least one gasket between at least one electrode frame and an ion exchange membrane in an electrolytic cell, said membrane comprising at least one layer of a material adapted for use as an ion exchange membrane and at least one layer of a material adapted to reinforce the membrane, said reinforcing layer being secured to at least one side of the membrane around the gasket-bearing peripheral surface of the membrane; and

(b) applying a compressive force to the cell.

Fig. 1

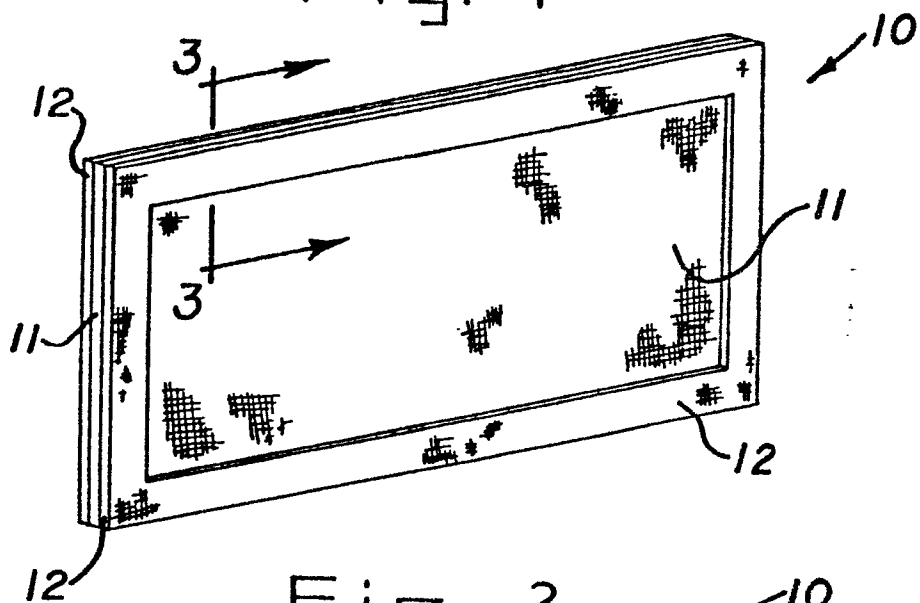


Fig. 2

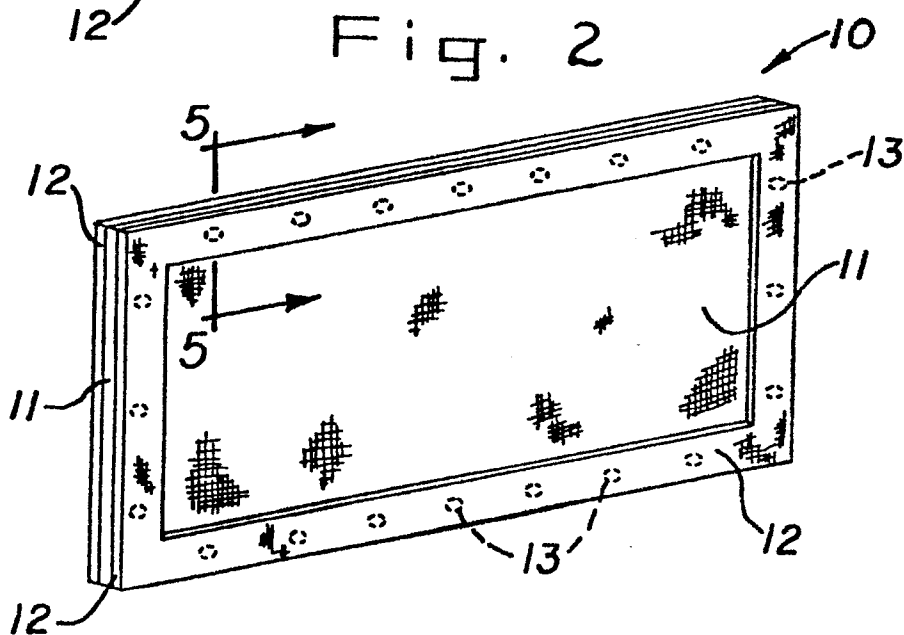


Fig. 3

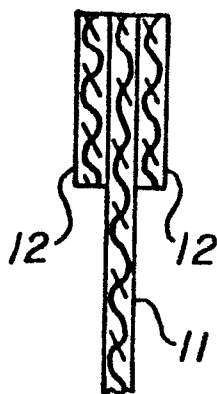
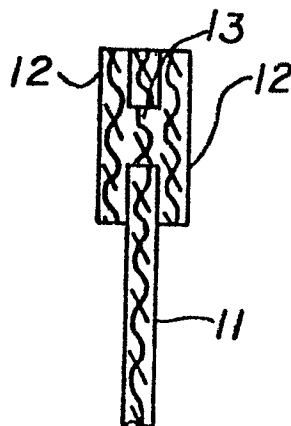
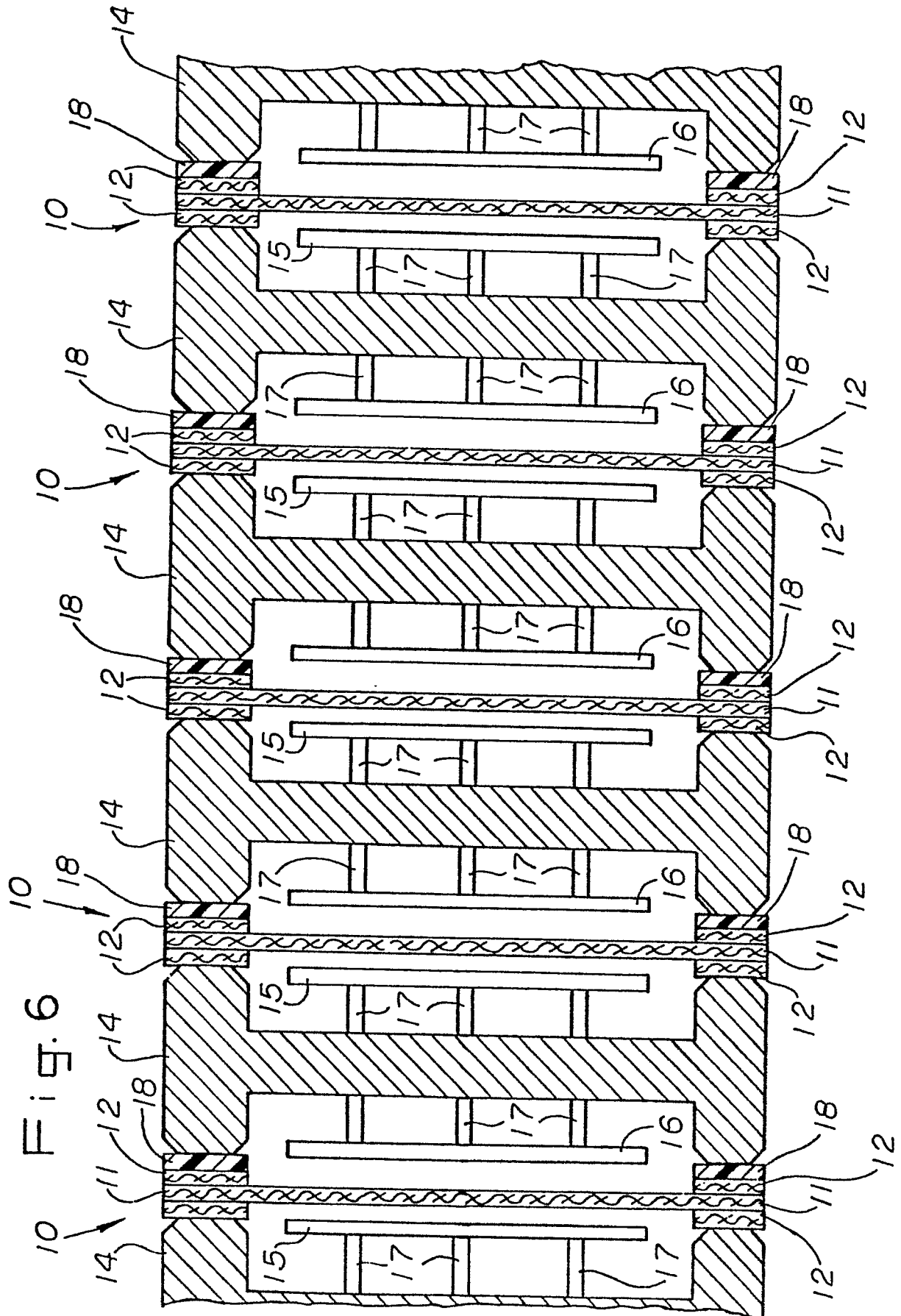


Fig 4



Fig 5







European Patent
Office

EUROPEAN SEARCH REPORT

0183096
Application number

EP 85 11 4059

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	GB-A-2 013 242 (KANEKAFUCHI CHEMICAL) * Page 2, lines 70-78 *	1,2,4, 6,7	C 25 B 13/00 C 25 B 9/00
X	FR-A-1 540 964 (MONSANTO) * Page 1, right-hand column, lines 34-42; page 2, left-hand column, lines 1-17, right-hand column, lines 4-38; page 3, claims; figure 2 *	1,5,7, 8	
A	EP-A-0 051 380 (OLIN CORP.) * Figures 1,2 *	1	
A	DE-A-2 821 983 (HOOKER) * Figures 2,5,6 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 25 B 13 C 25 B 9
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-02-1986	Examiner GROSEILLER PH.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			