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DIAPHRAGM FOR USE IN ELECTROLYSIS

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FIG-1

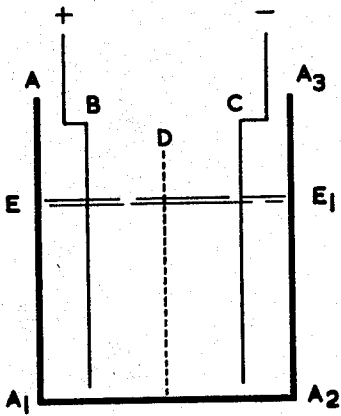


FIG-2

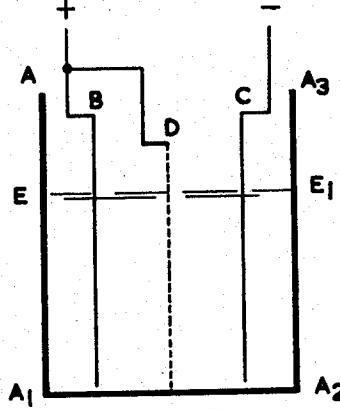
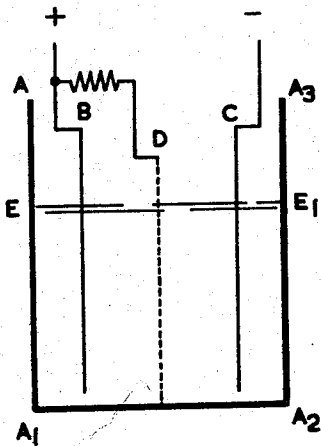


FIG-3



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## DIAPHRAGM FOR USE IN ELECTROLYSIS

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4 Claims. (Cl. 204—1)

This invention relates to a diaphragm for use in carrying out electrolyses.

As is known such diaphragms have for their purpose to keep the products formed during the electrolysis separated from each other and to prevent undesirable by-reactions, though the diaphragm is to allow the ions to pass unhindered.

Usually porous materials of inorganic or organic nature are used for diaphragms. The diaphragms of the first mentioned type which, for example, consist of asbestos, fritted glass, earthenware, etc., must be rather thick if they are to have a sufficient mechanical strength. The result thereof is that the diaphragm will have a large ohmic resistance and the potential differences on either side of the diaphragm are not inconsiderable. This results inter alia in large losses in current and undesirable reactions. The organic materials, such as cellophane, parchment, canvas, etc., are occasionally used as diaphragms, but the drawback attaching to these materials is that they have little chemical resistance and a slight mechanical strength. Furthermore a perforated diaphragm from noble metal has been proposed, which is chemically resistant and which also in a thin form has a sufficient mechanical strength, but a great disadvantage is that it will give rise to induction so that the diaphragm is charged and a discharge of ions and other secondary reactions will take place in the electrolysis cell in place where this is undesirable.

The invention is based on the insight that diaphragms may advantageously be manufactured from a porous metal, the surface of which can easily be provided with a layer insulating the subjacent metal from the passage of current therethrough and which is inert in respect of the electrolyte. Such a layer will be called a "barrier layer," hereinafter.

The diaphragm according to the invention is characterized therefore in that it comprises a core of a porous metal having its surface provided with a barrier layer entirely or substantially preventing the passage of current, which barrier layer is insoluble in the electrolyte.

Some metals having this property are, for example aluminium, bismuth, zirconium, tantalum and titanium. Of the above mentioned metals titanium is to be preferred because in substantially all electrolytes a barrier layer will form on titanium, the only exception being electrolytes containing fluorine. On the majority of the other metals mentioned a properly sealing and resistant barrier layer will only form if oxygen is evolved at the anode.

The barrier layer may be provided in simple manner, e.g. by anodic oxidation. The barrier layer thus obtained may still be strengthened by a thermal and/or chemical treatment. For example, the diaphragm can be heated in an oxygen containing atmosphere to form an oxide of titanium, in a nitrogen containing atmosphere to form a nitride of titanium, and in a chlorine containing atmosphere to form a chloride of titanium. The heating may be from 400 to 800° C. for period up to 6 hours.

The diaphragm according to the invention inter alia has the following advantages. It is chemically resistant and its mechanical strength is of such a nature, that the

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thickness of the diaphragm need only amount to a fraction of one millimeter. As a result the pores are substantially rectilinear in contradistinction to e.g. a diaphragm of asbestos which has no rectilinear pores so that the current is to cover a long path and the resistance is increased. In addition the diaphragm according to the invention admits of being easily worked and of being given the desired shape.

In carrying out an electrolysis by means of a diaphragm according to the invention said diaphragm may be placed in a conventional manner midway between the anode and the cathode in the electrolyte. It may be advantageous to conductively connect the one side of the diaphragm directed towards the anode, with the anode, so that the diaphragm during the electrolysis is continuously alive and the barrier layer is continuously maintained.

It has been found that in the latter case the pores in the diaphragm may be large while substantially no intermingling of the liquid on either side of the diaphragm takes place. As a result of the presence of large pores the resistance in the diaphragm is smaller, so that a better useful effect is obtained.

We found that in carrying out an electrolysis by means of a diaphragm according to the invention a considerable saving in the watt-consumption is obtained.

The core metal of the diaphragm according to the invention may be manufactured in a manner known per se e.g. by sintering metal powder, by etching a metal plate, by mechanically perforating a plate, etc. Thus it is possible to provide a plate of titanium with a thickness of  $\frac{1}{20}$  mm. on either side with a layer of wax, whereupon the layer of wax is mechanically removed in a great number of places, the bared metal surface being etched with a hydrogen fluoride solution.

The invention will now be further elucidated with reference to the accompanying drawing schematically showing various embodiments of a diaphragm according to the invention. In said drawings A, A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, designate an electrolysis vessel, B an anode, C a cathode, D the diaphragm according to the invention and EE<sub>1</sub>, the level of the electrolyte in the vessel. The electrolysis vessel is made of insulated metal. The electrodes consist of known material.

In FIGURE 1 the diaphragm is not connected to the anode. The porous core material of the diaphragm, e.g. titanium, has been electrolytically provided with a barrier layer e.g. by the electrolysis of an aqueous solution of sodium sulphate or hydrochloric acid, the titanium plate being used as anode. The barrier layer may be strengthened by a thermal and/or chemical treatment.

In FIGURE 2 a diaphragm is shown which is of the same type as the diaphragm according to FIGURE 1, which diaphragm, however, is connected to the anode, so that during the electrolysis it is alive while the barrier layer is continuously maintained.

FIGURE 3 shows a similar construction as FIGURE 2, the difference being that there is a permanent or regulable resistor between the diaphragm and the anode, so that the voltage applied to the diaphragm may be adjusted at will. In FIGURE 3 the voltage applied to the diaphragm is lower than the voltage applied to the anode. If the voltage applied to the diaphragm should be higher than the voltage applied to the anode the diaphragm is connected to the source of current and the voltage of the anode can be controlled by means of the resistor.

The invention is not limited to a diaphragm of titanium. Also other metals forming a barrier layer resistant in the electrolyte used may be used according to the invention.

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I claim:

1. A method of carrying out electrolysis in which it is desired to keep two portions of the electrolyte separated yet allow ions to migrate to the electrodes, comprising placing a diaphragm of a metal selected from the group consisting of titanium and titanium alloy, said diaphragm having pores therethrough of a size such that substantially no intermingling of liquids on opposite sides thereof can take place and having a barrier layer of titanium oxide thereon, between an anode and a cathode in an electrolysis apparatus, placing a non-fluoride containing electrolyte on opposite sides of the diaphragm, passing a current from the anode to the cathode through the electrolyte portions and the diaphragm, and supplying anodic current to the diaphragm for continuously maintaining the barrier layer thereon.

2. The method as claimed in claim 1 in which the step of supplying anodic current to the diaphragm comprises supplying the current through a variable resistance, whereby the current can be varied.

3. An apparatus for carrying out electrolysis in which it is desired to keep two portions of the electrolyte separated yet allows ions to migrate to the electrodes, comprising a diaphragm of a metal selected from the group consisting of titanium and titanium alloy, said diaphragm

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having pores therethrough of a size such that substantially no intermingling of liquids on opposite sides thereof can take place and having a barrier layer of titanium oxide thereon, an anode and a cathode on opposite sides of said diaphragm, a container for electrolyte in which said diaphragm and electrodes are mounted, and current supply means connected to said anode and diaphragm and current supply means connected to said cathode for passing anodic current from the anode to the cathode.

4. An apparatus as claimed in claim 3 in which the current supply means connected to said diaphragm includes a variable resistance.

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