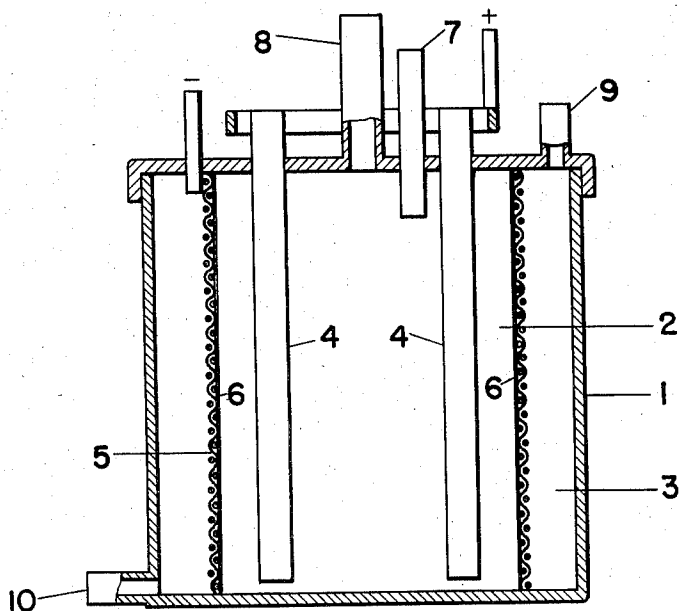FIG. I
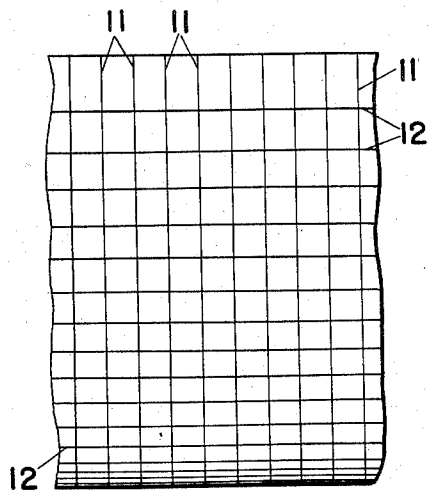
FIG. 2
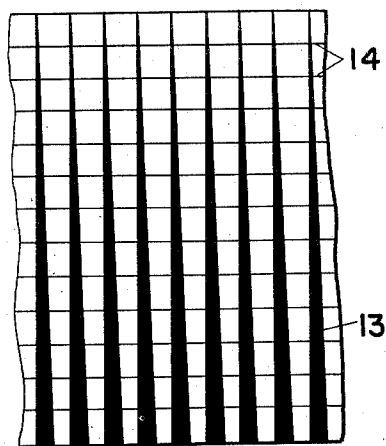
FIG. 3

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BY

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DIAPHRAGM CELLS

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5 Claims. (Cl. 204—252)

This invention relates to electrolytic diaphragm cells and more particularly to improvements in the diaphragm of such cells.

Electrolytic cells with vertical diaphragms suffer from the drawback of a non-uniform flow through the diaphragm caused by differences in hydrostatic pressure on either side of the diaphragm at the various levels of the cell. This is particularly true in cells in which the anolyte and catholyte differ substantially in specific gravity, the greatest problem being present in cells that are designed to run with an empty cathode compartment, such as certain caustic and chlorine cells. In cells of this type the percolation rate of the electrolyte through the diaphragm from one compartment to the other may reach a value three to four times higher at the bottom than at the upper part of the cell.

The present invention is particularly adapted to cells having a substantially empty cathode chamber, such as certain electrolytic cells for the production of sodium hydroxide and chlorine, though not limited thereto. The invention will, therefore, be described as applied to electrolytic diaphragm cells operating with a substantially liquid free cathode chamber, adapted to produce sodium hydroxide and chlorine from aqueous sodium chloride solutions. A schematic sketch of a cell of this type is illustrated in Figure 1 of the drawings.

In chloralkali cells, the flow of brine through the diaphragm is necessary to check the migration of the OH ions to the anode. The migration velocity of these ions, for example, is 0.018 cm./second at a potential drop of 1 v./cm. at 18° C. The percolation rate of the electrolyte through the diaphragm should, therefore, be adjusted to counteract this migration according to the desired density and current efficiency of operation. In practice, flows in excess of the figure calculated from ionic migration velocities are needed because of mechanical defects in the diaphragm, non-streamline flow, etc.

Due to the different hydrostatic pressure prevailing at the various levels of the anolyte, the ideal flow or percolation rate with a conventional diaphragm can be obtained at only one level hereinafter referred to as the "neutral zone." Above this level the percolation rate is too slow to counteract migration of the OH ions, while below this level the percolation rate is sufficiently rapid to carry substantial amounts of dissolved chlorine through the diaphragm. As a result, in the upper levels of the cell the alkaline area shifts towards the anode causing a lower current efficiency and the formation of chlorates, while near the bottom of the cell the chlorinated brine percolating to the cathode compartment forms hypochlorite which causes corrosion of the cell as well as reducing the current efficiency. Also, the diaphragm, which is generally made of asbestos, is in a highly alkaline medium in the upper portion of the cell and is in an acid medium in the lower portion of the cell.

Asbestos is attacked by hot alkali solutions, and asbestos leached by sodium hydroxide is susceptible to attack by acid brine. As a result, the life of the diaphragm,

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which is generally made of asbestos, is substantially shortened. Where there are fluctuations in cell operation, i. e. variations in voltage, variations in pressure in the chlorine and hydrogen lines, etc., the so-called "neutral zone" tends to shift during operation. This subjects a portion of the asbestos diaphragm, which has been weakened through leaching by alkali, to attack by the acid brine and the life of the diaphragm is still further shortened.

The problem of diaphragm life and uniformity of operation is further complicated by the fact that asbestos paper is substantially weakened when wet and is subject to failure because of this.

To prevent these conditions, various devices have been conceived. Attempts have been made to solve the problem by varying the size of the perforations in the cathode so that a substantially uniform percolation rate through the cathode is obtained. However, in order to obtain a uniform percolation rate through the cathode the removed portion of the cathode must be so small, particularly in the lower area, that a substantial amount of the hydrogen formed is prevented from escaping through the cathode. Also, the active cathode area must be substantially less near the upper part of the cathode than near the lower part of the cathode. It has further been proposed to increase the thickness of the diaphragm towards the bottom. However, there is substantially more material and labor required for this type of diaphragm; it is difficult to obtain the proper taper, and the electrical resistance is increased proportionately to the thickness of the diaphragm, other factors being constant.

I have now solved this problem of non-uniform percolation rate through the diaphragm, and at the same time have obtained a diaphragm of substantially increased strength by marking on the diaphragm surface a pattern which blocks out different areas of the diaphragm, the pattern being such as to make the permeability of the diaphragm inversely proportional to the hydrostatic pressure head encountered in the cell. The marking material used serves two purposes. It makes certain portions of the diaphragm impervious to the electrolyte and thus enables control of the percolation. It binds the asbestos fibers together so as to form a strengthening pattern on the diaphragm. This helps to maintain the shape of the diaphragm when wet.

In the drawings:

Figure 1 is a schematic view of a chlorine cell;

Figure 2 is a section of a diaphragm showing one type of marking; and

Figure 3 is a section of a diaphragm showing a different type of marking.

Referring to the cell of Figure 1, 1 is the cell casing which has an anolyte chamber 2 and catholyte chamber 3. Anodes 4, which are generally made of graphite, project downwardly into the cell and are surrounded by an iron perforated cathode 5. An asbestos diaphragm 6 is placed between the anode and cathode against the cathode. The brine electrolyte is brought into the cell through inlet 7. The chlorine is removed through outlet 8, the hydrogen through outlet 9, and the sodium hydroxide solution through outlet 10.

The diaphragm as shown in Figures 2 and 3 has marked thereon a pattern which provides uninked areas which progressively increase in size from the bottom to the top. In Figure 2, the pattern consists of a series of vertical inked lines 11, crossed by a series of horizontal inked lines 12. The vertical lines 11 are equally spaced whereas the spacing between the horizontal lines 12 progressively increases with increased distance from the bottom. In Figure 3 the pattern is formed by vertical lines 13. These progressively decrease in width from the bottom towards the top. For further strength horizontal lines 14 may be added. Any pattern can be used which

will block out progressively larger areas of the diaphragm approaching the bottom. However, those patterns are preferred which give the greatest supporting strength to the diaphragm. Thus, the preferred patterns are formed by crossing lines, the simplest and most easily calculated being the series of rectangles shown in Figure 2.

The patterns can be drawn on the diaphragm or can be printed by any suitable printing apparatus. Since, for controlling the percolation rate it is only necessary that the design appear on one side of the asbestos diaphragm, the thickness of the paper on which the design is marked is not particularly critical. For greatest strength and life of the diaphragm, however, and for preferred operation, the design should appear on the side of the diaphragm which is facing the anode and is in direct contact with the main body of the electrolyte. The actual diaphragm may be built up of several layers of asbestos paper until a diaphragm of the desired thickness has been obtained. In such a case only one layer of asbestos paper need have the design marked thereon to obtain uniform percolation though other layers can be so marked if desired. If the layer so marked is the one nearest the anode and the surface facing the anode is marked, then the markings will help to strengthen the whole diaphragm since the asbestos will be held between the printed lattice and cathode. In practicing the present invention it is therefore preferred that the layer closest to the anode always be marked even though other layers of the diaphragm may contain the described markings thereon.

Various methods may be used for arriving at the size of the areas on the diaphragm surface to be left open. The following, however, is the preferred method.

The percolation rate for different hydrostatic pressure heads is first obtained for the diaphragm paper which is to be used. This is plotted and the resulting curve is used in calculating the size of the open areas in the diaphragm. In a specific example the following figures were obtained:

Hydrostatic Pressure/Inch	7	15	19	25
Percolation Rate, cc./h./dm.²	88	200	253	300

The values are only relative since, in the particular case, they were obtained by using distilled water. The conditions which exist in a cell in operation are too complicated to reproduce experimentally in obtaining percolation rates and, apparently, are not necessary.

On the basis of the curve obtained from the above figures a second curve was prepared representing a uniform permeability. This was done by assuming the percolation rate and time as constant, the area as variable and substituting in the formula:

$$AP = \text{constant}; \quad A = \frac{\text{constant}}{P}$$

P represents the percolation rate at varying hydrostatic pressures and A the area which would be required to keep the flow rate constant. Substituting the percolation data previously obtained in this equation, values can be obtained for a new graph representing the areas required to keep a uniform percolation at the various levels.

In order to obtain a unit area at approximately the middle of the diaphragm, approximately 30″ high, that would represent a unit, the value of the percolation rate, 200 cc., at a hydrostatic pressure head of 15″ is used, as a base figure. Substituting this in the equation, one obtains the area changing factor or the relative variation in area that must exist at the different hydrostatic pressure levels to obtain a uniform percolation.

For example, at 15″ the area is represented as a unit

$$A = \frac{200}{200}$$

At 7″ the area must be 2.26 times that at 15″; i. e.,

$$A = \frac{200}{80} = 2.26$$

In a similar way the following values were obtained:

Hydrostatic Pressure/Inch	7	15	19	25
Percolation Rate, cc./hr./dm.²	88	200	253	300
Area Changing Factor	2.26	1.0	0.78	0.66

If a diaphragm with rectangular markings is to be prepared the simplest method of preparation is to first assume definite dimensions for the unit area at the 15″ level. A suitable choice is ¼″ x ¼″. The diaphragm is then marked with parallel vertical lines ¼″ apart giving a constant width to all areas. Now by multiplying ¼″ (.25) by the area changing factor for any hydrostatic pressure height, the spacing between the horizontal lines for that height to give uniform percolation can readily be determined. Thus the spacing at 7″ would be .25″ x 2.26 or .565″.

Any marking material may be used which is resistant to the cell liquor, which will render the marked areas more impervious to fluid flow and which will form a strengthening pattern when marked on the diaphragm.

Among the materials that have been found suitable for this purpose are chlorinated rubber, chlorinated and chloro-sulfonated polyethylene, highly chlorinated or fluorinated hydrocarbons, polyvinyl, polyvinylidene and acrylic latexes. The following are illustrative ink formulations:

	Percent
Parlon 10 C. P. (chlorinated rubber, Hercules)	10
Halowax 4005 (chlorinated paraffin 70% Cl)	40
Halowax 4003 (chlorinated paraffin 40% Cl)	5
Stabilizer A5	2
Solvent (mixture of methyl Cellosolve and acetone)	43

Exon 400 XR61 (a fluorocarbon resin)	7.0
Halowax 4005	40.0
Halowax 4003	2.0
Stabilizer A5	1.0
Solvent (mixture of methyl Cellosolve and acetone)	50.0

Diaphragms prepared in accordance with the present invention were tested in regular chlorine cell operation over substantial periods of time. The printed diaphragms used were about ⅔ the thickness of the diaphragms used in the non-test cells producing commercial chlorine. This represents a substantial saving in asbestos. The voltage of the cells with the printed diaphragms was about 8 to 10% lower than that of adjacent cells equipped with regular diaphragms. This resulted in an 8 to 10% saving on power. Yet the strength of the lye obtained from the test cells using the printed diaphragm was within the same range as that of the other cells. None of the cell containers using the printed diaphragms showed any signs of internal corrosion and no hypochlorite was noted in the lye or excessive hydrogen in the chlorine gas produced. The cells were opened and tests were made of the lye concentration at various levels. These tests indicated that the flow rate of the cell liquod through the diaphragm was substantially uniform.

In describing the present invention the diaphragms have been described as used with chlorine cells of the empty cathode compartment type. However, the invention is not limited to cells of this type but the marked diaphragms of the present invention may be used to advantage in any cell where non-uniform flow rate through the diaphragm, due to differences in hydrostatic pressure, is a problem.

Having thus described my invention, I claim:

1. In an electrolytic diaphragm cell comprising an anode, a cathode, an anolyte chamber and a catholyte

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chamber, a preformed pervious diaphragm arranged substantially vertically between the anode and the cathode and having a series of impervious lines dividing the area of the diaphragm into pervious spaces which are progressively smaller from the top to the bottom of the diaphragm to produce a uniform percolation rate throughout the area of the diaphragm.

2. The diaphragm of claim 1, in which the lines form a series of rectangles that decrease in size from the top to the bottom of the diaphragm.

3. The diaphragm of claim 1, made of asbestos with the lines drawn thereon.

4. The diaphragm of claim 1, made of asbestos with the lines printed thereon.

5. The diaphragm of claim 1, in which the lines are formed of a member of the group which consists of chlorinated rubber, chlorinated polyethylene, chlorosulfonated polyethylene, highly chlorinated hydrocarbon, highly fluorinated hydrocarbon, polyvinyl latex, polyvinylidene latex and acrylic latex.

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UNITED STATES PATENT OFFICE
Certificate of Correction

Patent No. 2,860,100   November 11, 1958

Leszek Jan Konrad Krzyszkowski

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 2 and 3, for that portion of the equation reading

$$A=\frac{200}{80}=2.26 \qquad \text{read} \qquad A=\frac{200}{88}=2.26$$

line 63, for "liquod" read —liquor—.

Signed and sealed this 31st day of March 1959.

[SEAL]

Attest:

KARL H. AXLINE,

Attesting Officer.

ROBERT C. WATSON,

Commissioner of Patents.