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R. D. BLUE ET AL

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CHLORINE CELL HAVING PROTECTED DIAPHRAGM

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2 Sheets-Sheet 1

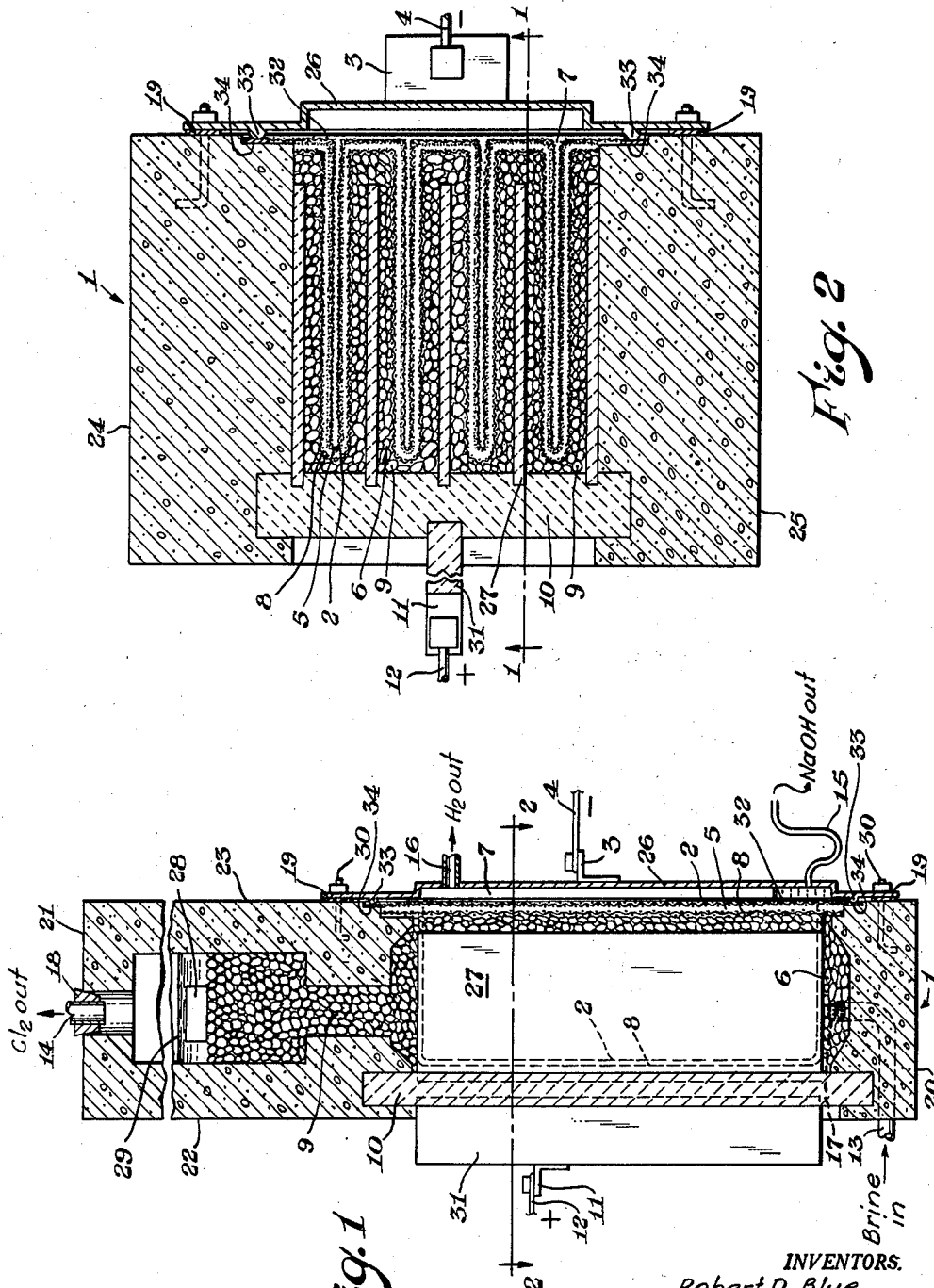


Fig. 2

Fig. 1

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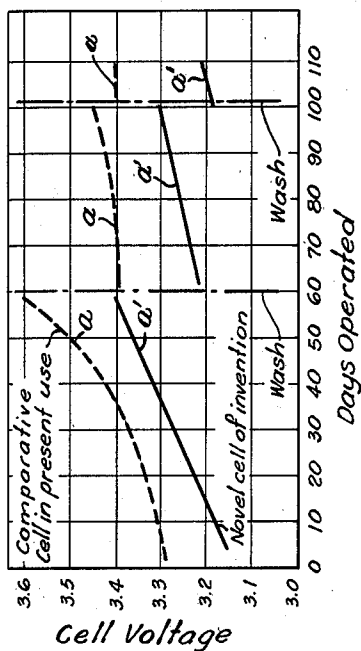
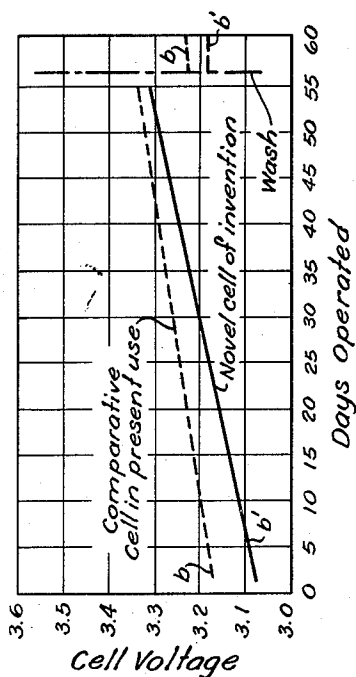
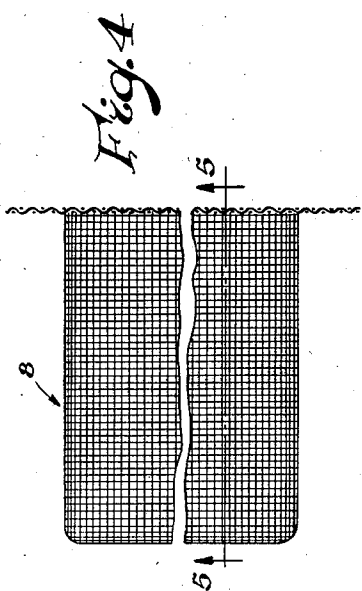
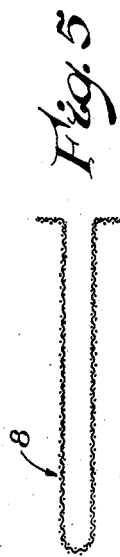
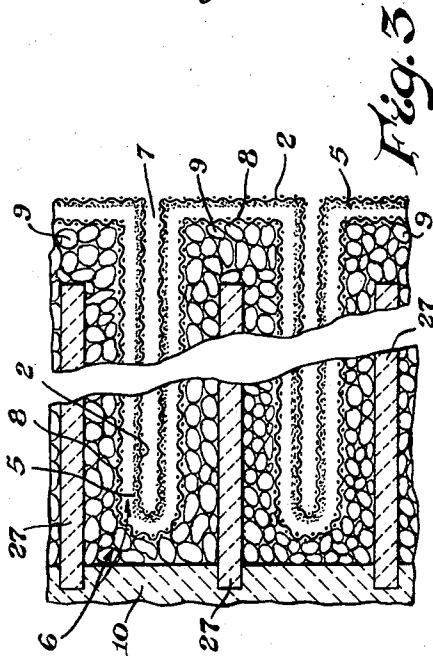
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CHLORINE CELL HAVING PROTECTED
DIAPHRAGM

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This invention relates generally to the diaphragm type electrolytic cell for the production of chlorine and particularly relates to such cell having a protective grating or screen positioned adjacent to and substantially parallel to the diaphragm on the anode side thereof and having an anode of carbon or graphite particles adjacent to the protective screen.

A well-known method of producing chlorine is by the electrolysis of the chloride of an alkali metal, e.g., sodium chloride from an aqueous solution, in an electrolytic cell, and collecting the chlorine at the anode and hydrogen and a solution containing the corresponding alkali hydroxide, e.g., sodium hydroxide, at the cathode.

Chlorine interacts with the alkali hydroxide formed if no provision is made to prevent such interaction. Such interaction in a chlorine-producing cell reduces the efficiency of the cell for a number of reasons, among which are: loss in recovery of chlorine and alkali hydroxide; formation of alkali hypochlorites and ultimately chlorates, the presence of which are undesirable; the formation of oxygen which in turn attacks the carbon of the anode to form carbon dioxide; contamination of the alkali hydroxide; and increased power consumption and as a consequence thereof, increased costs per unit of chlorine and alkali hydroxide produced.

It is known to place a diaphragm between the anode and cathode in an effort to prevent this interaction. The diaphragm must be of a material which is permeable to the electrolyte, substantially resistant to the action of both the alkali hydroxide and the wet chlorine, and sufficiently strong to withstand the stresses associated with such use. Such cells are commonly known as diaphragm-type cells and will be so referred to herein.

Among the materials which have proved most successful when used in such diaphragms is asbestos. The asbestos has been used in the form of paper, woven fabric, and pulp made to adhere to a cathode. In the last instance, the cathode is formed of perforated metal or wire mesh and the asbestos, from a thick aqueous slurry, is drawn against the perforated cathode by means of suction and thereafter made to adhere thereto by drawing out most of the remaining water and partially or completely drying the asbestos in situ. The use of such diaphragms, however, has not been entirely successful.

Heretofore, chlorine cells have employed anodes in the form of solid blocks or in the form of shapes firmly attached together. Although when the cell was put in operation the solid anode was placed very close to the diaphragm and the space between the cathode and anode was separated by an interelectrode distance equal only to the thickness of the diaphragm plus sufficient space for the brine to circulate therethrough, the anode was gradually consumed or eroded away particularly along the surface facing in the direction of the cathode. Therefore, as the cell continued in operation, the distance between the anode and cathode increased throughout the operation. As a result of the increase of the interelectrode distance, the resistance to electrical flow also in-

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creased, resulting in increased power consumption and cost of producing chlorine and the hydroxide.

We have invented an improved electrolytic cell for the production of chlorine having a diaphragm therein of a known material, e.g., asbestos, vertically positioned in the cell between the anode and the cathode so as to divide the cell into an anolyte and a catholyte compartment, the improvement consisting of a protective perforated sheet, or meshed grating or screen, having the exposed surfaces coated with a non-conducting resinous material inert to the reactants of the cell, said sheet or screen being positioned substantially parallel and adjacent to or abutting said diaphragm on the anode side thereof, and that portion of the anode adjacent to the sheet or screen consisting of compact particles or fragments of graphite or amorphous or baked carbon which are prevented from directly contacting the diaphragm by the protective sheet or screen.

The portion of the anode farthest removed from the protective screen preferably consists of a solid shape of graphite and serves to hold the particles of graphite or carbon in position against the protective screen and to supply a positive electrical charge to the mass of particles. The solid shape has a terminal attached thereto leading to a positive source of electricity.

The cathode, as is commonly employed in conventional chlorine-producing cells, is formed of a metal screen. It may comprise a substantially flat screen or it may comprise a series of sinuous repeating folds or fingers, each fold or finger being in a vertical plane and about 2 to 3 inches from center to center of each fold. The asbestos diaphragm is firmly adhered to the cathode. If the cathode is comprised of a series of folds, the novel protective screen of the invention is shaped so that it follows the contour of the cathode, being separated therefrom by the asbestos diaphragm.

The cell of our invention provides means for producing chlorine and an alkali hydroxide by the electrolysis of an alkali chloride which operates at a lower and less variable voltage, at a lower anode cost, and at a lower power consumption per pound of chlorine and alkali hydroxide produced, and which requires less frequent dismantling and cleaning of the cell than diaphragm type chlorine cells heretofore known.

The protective screen, which comprises the novel features of the cell of our invention has openings in it which preferably comprise at least half of its area. The openings are smaller than the graphite or carbon particles of the anode and generally are between $\frac{1}{4}$ and $\frac{1}{2}$ inch along their greater dimension. The screen consists preferably of (1) an inner structural material which is composed of either strands, fibers, filaments, or cords, which may be derived from either natural or synthetic sources, and (2) an outer adhesive coating consisting of a polymer which imparts added structural strength and which renders the screen non-conductive of electric current and highly resistant to chemical attack and to the excessive absorption and softening effect of caustic, acidic, or salt solutions. As an alternative construction, the novel protective screen may consist of a pressed or molded sheet of non-conducting and chemically resistant polymer. The preferred polymer is a polymerized fluoro- or fluorochloro-substituted ethylene resin. Examples of the polymers contemplated by the invention are polytetrafluoroethylene and polymonochlorotrifluoroethylene. Other satisfactory polymers are electrically non-conducting synthetic rubbers.

If an anode consisting partially of particles or fragments of graphite or carbon is attempted to be used without employing the novel protective screen of the invention, some of the particles adjacent to the diaphragm become enmeshed in the caustic-soaked diaphragm and

set up local electrolytic side reactions resulting in the formation of alkali carbonate in the cell effluent and CO_2 in the chlorine gas by the electrolysis of the alkali hydroxide in the diaphragm.

In the practice of the invention, we prefer to fabricate the structural material into an interwoven or meshed configuration and thereafter treat said material with an aqueous dispersion of the polymer as by a dipping, spraying or brushing application and thereafter cure in accordance with the recommended procedure for such polymer.

As an alternative to the preferred practice of the invention, the individual untreated fibers may be treated with the polymer and cured prior to fabrication and thereafter fabricated into the screen of the invention. As a second alternative, the protective screen may consist of the above polymer formed into a self-supporting continuous pressed sheet having perforations therein, cured, and positioned in the cell in accordance with the invention.

The annexed drawing shows one form of the cell of the invention.

Fig. 1 of the drawing is a side elevational view, taken on line 1—1 of Fig. 2, in section.

Fig. 2 is an enlarged horizontal section of the cell of Fig. 1 on line 2—2 of Fig. 1.

Fig. 3 is an enlarged fragmentary portion of the cathode assembly of Fig. 2.

Fig. 4 is an elevational view of the novel protective screen of the cell of Fig. 1.

Fig. 5 is a section of the protective screen on line 5—5 of Figure 4 showing one fold of the screen.

Figs. 6 and 7 are graphs which show voltages required in the cell employing the novel features of the invention in comparison to voltages required by cells which do not employ such novel features but are otherwise comparable. The effect on voltage consumption brought about by washing both types of cell is also shown.

Referring to the drawing in more detail, there is shown a cell of the invention having concrete body structure 1, bottom 20, top 21, front wall 22, rear wall 23 and opposing parallel side walls 24 and 25. Openings are provided in concrete walls 22 and 23.

Vertically positioned in structure 1 just inwardly of the opening provided therefor in wall 23 is metal cathode 2 which has flattened border 34 thereabout. Adhering to cathode 2 on the anode side thereof is asbestos diaphragm 5 which separates the cell into anolyte compartment 6 and catholyte compartment 7. Adjacent to and substantially following the contour of asbestos diaphragm 5 on the anode side thereof is novel protective coated grating or screen 8. Asbestos diaphragm 5 is thereby positioned between cathode 2 and screen 8. Covering the opening in wall 23, as defined by wall edge 32, is plate 26. Plate 26 has ridge 33 thereon which follows the general outline of wall edge 32 and which is raised inwardly toward border 34 of cathode 2. Studs 30 secure plate 26 to wall 23 and also hold ridge 33 of plate 26 in firm contact with border 34 of cathode 2. To plate 26 is attached terminal 3 which in turn makes contact with negative lead-in line 4 attached to a source of direct current. Plate 26, therefore, serves as both the outer inclosing wall of catholyte compartment 7 and a bus bar for carrying negative electricity to cathode 2.

In contact with screen 8 is anode graphite particle body 9 which is loosely compacted in anolyte compartment 6. Weight 28 maintains a compacting effect on particle body 9. Graphite block 10 is inserted in the opening provided therefor in wall 22. Graphite block 10 forms both outer wall of anolyte compartment 6 and a portion of the anode of the cell. Perpendicular to block 10 are horizontal extensions 27 which, together with block 10, insure good electrical contact with the body of graphite particles 9. Terminal 11 is secured to anode block 10 by means of contact bar 31 and has positive lead-in line 12 attached thereto.

Inlet pipe 13 in bottom 20 provides for the ingress of an aqueous solution of an alkali chloride, referred to hereinafter as brine, into anolyte compartment 6. Outlet 14 in top 21 provides for an escape of chlorine gas evolving at the anode. In plate 26 is pipe 15 for egress of the alkali hydroxide and outlet 16 for escape of hydrogen gas and other gases, if any, from catholyte compartment 7. Strainer 17, positioned in pipe 13 at its entrance to anolyte compartment 6, retains the particles of graphite in compartment 6 and yet permits entrance of fresh brine thereto through pipe 13. Gasket 18 provides a snug fit between outlet 14 and the opening provided therefor in top 21. Gasket 19 provides a snug fit between the plate 26 and wall 23 about the opening defined by wall 32.

The novel grating or screen 8 shown in the drawing was made by cross-weaving $\frac{1}{16}$ inch asbestos cord at about $\frac{3}{8}$ inch center-to-center spacing and thereafter dipping the uncoated grating for about 5 seconds at room temperature, into about a 40 percent aqueous colloidal dispersion or suspension of polytetrafluoroethylene, e.g., Teflon latex. The coated grating was dried overnight at room temperature and then baked at 350°C . for about 15 minutes. It was then placed in position in the cell as shown in the drawing.

The anolyte compartment between anode block 10 and grating 8 was about $\frac{3}{4}$ inch in width where the folds of the cathode extend farthest toward block 10, i.e., at the narrowest width. The space thus formed was packed with graphite pieces which were generally spheroidal and about $\frac{1}{2}$ to $\frac{3}{16}$ inch in diameter.

To operate the cell of the invention, a brine consisting essentially of a concentrated salt solution, for example, about 315 grams of sodium chloride per liter of water, is pumped into anolyte compartment 6 through inlet 13. The electrolysis of the brine is started by setting up an electrical potential between anode particle body 9 and cathode 2 by attaching lead-in line 12 to the positive take-off of a D.C. source of electricity (not shown) and lead-in line 4 to the corresponding negative take-off of the same source of electricity. The brine is permitted to rise in anolyte compartment 6 until it is above the graphite particle body 9, when the brine flow is cut back so as to maintain level 29 above graphite particle body 9 and below that which would result in an overflow out through outlet 14.

The brine comes into contact with the anode comprising block 10 and particle body 9, but especially with the particles of graphite body 9 forming chlorine, and cathode 2, forming ultimately sodium hydroxide and hydrogen gas. The chlorine, thus formed, rises and passes out through outlet 14. The alkali hydroxide, referred to as the caustic, e.g., sodium hydroxide, thus formed, together with water from the brine and some undecomposed salt, flows to the bottom of the catholyte compartment 7 and passes out through outlet 15. The hydrogen rises and passes out through outlet 16. Asbestos diaphragm 5, since contact with particle body 9 is prevented by novel screen 8, prevents intermingling of products formed in the anolyte compartment with those formed in the catholyte compartment.

Diaphragm 5 in conjunction with novel screen 8 prevents both the combining of chlorine and hydrogen, which in the absence of separatory means often takes place with explosive violence, and prevents the reaction between alkali hydroxide and chlorine, which would result in the formation of the hypochlorite and later the chlorate. The chlorate, if formed, would attack the carbon of the anode to form CO_2 , cause excessive graphite consumption, contaminate the gaseous products with CO_2 and thereby lessen the efficiency of the cell. Such loss of efficiency is hereby prevented by the structure of the cell of the invention.

By referring to Figures 6 and 7 of the drawing, the decreased voltage requirement for cells constructed

according to the invention may be compared to cells which are presently in use. The broken lines represent voltages used by cells *a* and *b* which are of conventional construction; the solid lines represent voltages used by cells *a'* and *b'* which employ the novel features of the invention. Vertical lines designated "wash" represent washings of the asbestos diaphragm which were done after the number of days of continuous operation shown on the horizontal axis. The voltage required to operate the four cells are set out on the vertical axis and the days of continuous operation are set out on the horizontal axis of Figures 6 and 7.

The cells *a* and *a'*, the performance of which is shown in Figure 6, employed asbestos diaphragms formed by wet asbestos being drawn against the cathode screen before assembling the cells according to known practice and as described hereinabove. Cells *b* and *b'*, the performance of which is shown in Figure 7, employed asbestos paper of a thickness of about 0.05 inch according to known practice. Except for the novel features of the invention in cells *a'* and *b'* and the employment of drawn asbestos diaphragms in cells *a* and *a'* and paper asbestos diaphragms in cells *b* and *b'* the cells were of the same construction. The graphs show a reduced voltage consumption of 0.1 to 0.2 volt when the novel cell of the invention was used. Such reduced voltage substantially reduces the kilowatt hours of power consumed on a large scale operation and is of appreciable economic importance.

Additional advantages of the cells constructed according to the invention are present which are not apparent from examination of Figures 6 and 7. Among such advantages is the lower cost of graphite for the anode. In conventional cells, single graphite blocks or shapes are used. Therefore, in conventional cell operation, physical erosion and chemical reaction of the blocks occur which widen the spacing between anode and cathode, thereby increasing the cell resistance after protracted operation. In cells constructed according to the invention, graphite erosion and consumption are largely confined to the pieces which may be spheroidal, rod-shaped, or generally irregular in the nature of the particles forming body 9 of the drawing. Therefore, a spacing between the anode and cathode which is not substantially greater than the thickness of the diaphragm and the novel screen can be maintained for long periods of operation. Another advantage is that additional particles are readily added without dismantling the cell. Furthermore, the graphite particles are procurable at lower cost than are single specifically shaped graphite of relatively large size.

A further advantage to be derived from the practice of the invention is found by determining the percentage of carbon dioxide in the chlorine gas evolving from the anolyte compartment. In a conventionally constructed cell, the percentage of carbon dioxide was found to be in the range of 1.0 to 1.5 percent. In contrast thereto, the percentage of carbon dioxide was as low as 0.2 percent in the chlorine evolving from a cell which employed graphite particles in the anode and which contained the protective screen of the invention described hereinabove, but which was otherwise of comparable construction to a conventional cell.

It is understood that cells containing protective gratings or screens which are but modifications of the screen herein illustrated are within the teachings and scope of the invention. For example, a cell containing a protective grating composed of strands of metal, glass, or natural or synthetic fibers which are woven so as to permit permeation of brine for electrolysis between the strands, and which are coated, dipped, or otherwise impregnated with non-conducting, non-reactive polymer such as a polymerized halide-substituted ethylene, e.g., polytrifluoro-

chloroethylene (polymonochlorotrifluoroethylene) as described in U.S. Patent 2,686,738 or polytetrafluoroethylene as described in U.S. Patent 2,710,266 are within the scope of the invention. The preparation of a polymerized halide-substituted ethylene coating according to one of the above cited patents is only a suggested method. The polymer useful in the present invention is in no way limited by its method of preparation and may be prepared according to any method so long as the polymer produced is sufficiently structurally re-inforcing and is electrically non-conducting, and is non-reactive with the fluid ingredients of the cell.

Having described the invention, what is claimed and desired to be protected by Letters Patent is:

1. In an improved diaphragm-type chlorine cell for the electrolytic decomposition of a chloride brine in the production of chlorine gas containing a non-conducting diaphragm which has small resistance against distortion, perforation, and dislodgement from position and which divides the cell into an anolyte compartment and a catholyte compartment, the improvement comprising a substantially rigid screen composed of meshed filaments positioned parallel to and adjacent to said diaphragm for the protection of the diaphragm on the anode side thereof, the filaments of said screen being coated with a protective coating selected from the group consisting of polymerized monochlorotrifluoroethylene and tetrafluoroethylene, and an anode consisting of a body of particulate graphite of a minimum particle dimension greater than that of the meshes in said screen compacted in said anolyte compartment and resting against said screen, and a rigid graphite core adapted to be attached to a source of electrical energy extending into said body of particulate graphite.
2. An improved cell for electrolysis of brine comprising a cell chamber; a metal cathode within said chamber having openings therein for the passage of fluids therethrough; a fluid-permeable electrically non-conductive diaphragm which is easily distorted, perforated, and dislodged from position by contact with hard solid fragmented objects located adjacent to said cathode and dividing said chamber into a catholyte compartment and an anolyte compartment; a structurally self-supporting substantially rigid perforate sheet of polymer selected from the group consisting of polytetrafluoroethylene and polymonochlorotrifluoroethylene positioned substantially parallel to and adjacent to said diaphragm in the anolyte compartment; and an anode comprising a compact body of fragmented carbon selected from the group consisting of amorphous carbon and graphitized carbon in contact with said protective sheet, said fragmented carbon being of greater size than the perforations in said protective sheet and a rigid continuous electrically-conductive member in contact with the body of fragmented carbon.

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