Feb. 9, 1960 C. T. GALLINGER 2,924,558

FUSED SALT ELECTROLYSIS

Filed June 25, 1958 2 Sheets-Sheet 1

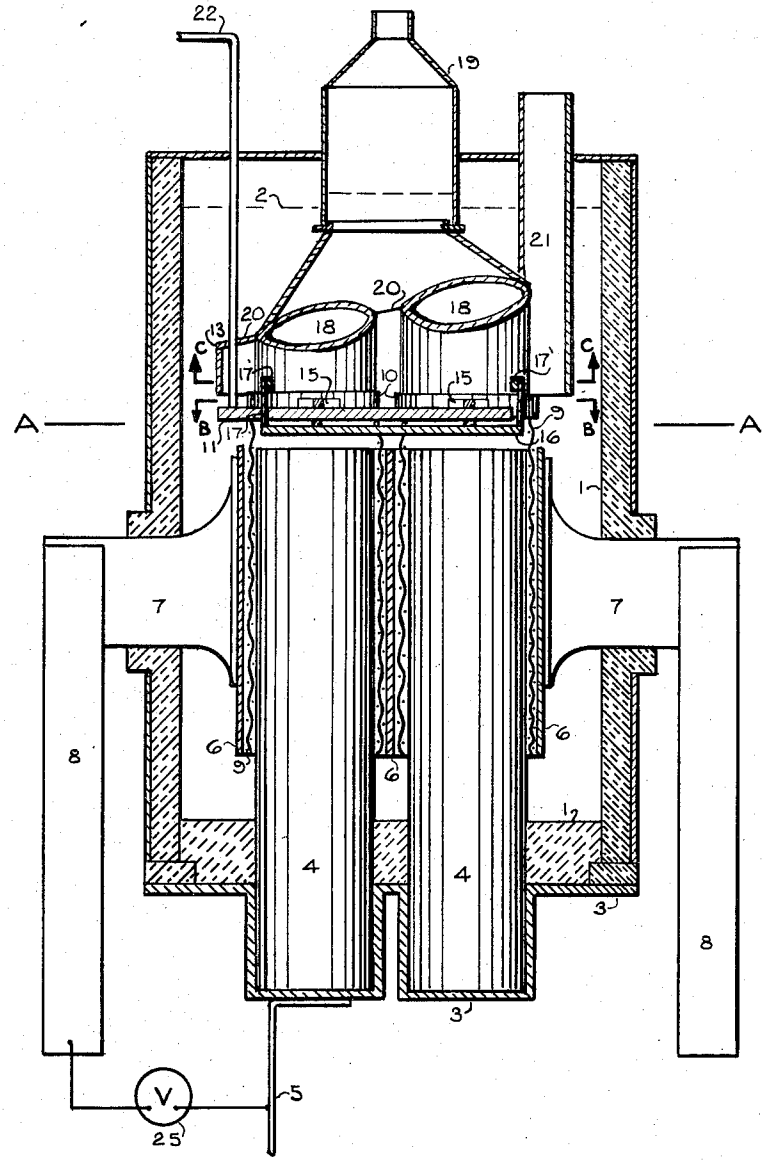


FIG 1

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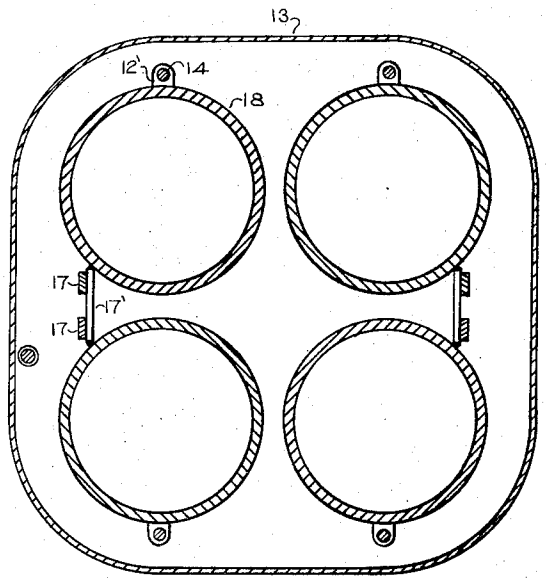


FIG 2

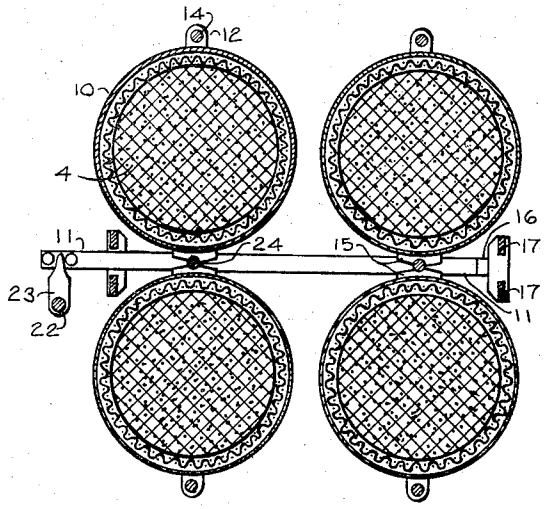


FIG 3

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United States Patent Office 2,924,558 Patented Feb. 9, 1960

2,924,558

FUSED SALT ELECTROLYSIS

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Application June 25, 1958, Serial No. 744,433

6 Claims. (Cl. 204—68)

This invention relates to improvement in apparatus and process for the production of alkali metal, particularly sodium, by the electrolysis of a fused salt bath.

The electrolysis of a fused salt mixture in a "Downs" type sodium cell such as was originally disclosed in U.S. Patent 1,501,756, July 15, 1924, requires the use of a diaphragm between the anode and the cathode. The diaphragm is usually a cylindrical wire mesh screen surrounding the submerged vertically dispersed cylindrical graphite anode. Since the bath offers considerable electrical resistance it is necessary to keep the distance between anode and cathode as small as possible, preferably below 3 inches. In order to operate at reasonable temperatures the electrolytic bath consists of a mixture of salts, principally the chlorides of sodium and of an alkaline earth metal, usually calcium. Operation of such a cell results in the formation of sodium at the cathode together with small amounts of alkaline earth metal as well as smaller amounts of other impurities usually solid and originating from the inevitable contaminants of the electrolyte by cell wall components, such as silicates and contaminants in the salts fed to the cell to maintain the bath level as electrolysis depletes it by the removal of elemental sodium and chlorine. These impurities, especially calcium are usually solids and electrical conductors at cell bath temperatures. Generally the cell bath temperature will be between about 575° and 615° C. These solids, for reasons not too well understood, tend to accumulate in various areas between the diaphragm and the cathode thereby causing electrical shorts which often result in perforation of the diaphragm. Of even greater importance is the loss of production which is directly proportional to the extent of the electrical short and ceases entirely if, as often happens, the current must be interrupted to permit correcting the difficulty. If the solid between the diaphragm and the cathode is not dislodged it will continue to accumulate and necessitate a temporary interruption of the current while the collector system together with the diaphragm suspended therefrom is removed and the diaphragm replaced with a new one.

The only method heretofore available for dislodging the shorting solid material between the diaphragm and the cathode short of removal of the diaphragm involved shaking the entire collector system such as by the use of a bar or the like tool. This rather rough treatment often resulted in distorting the diaphragm so that a direct short caused by a part of it touching an electrode necessitated replacement with a new diaphragm and this also involved removal of the collector system, replacement of the diaphragm, recentering the collector-diaphragm assembly in a dummy cell and then replacing the assembly in the cell for resumption of operation. But not only are these "shaking," and replacement operations costly in the loss of production time they are also very hazardous to operating personnel. And another problem with shaking the collector-diaphragm assembly to dislodge adhesions and also with replacing the diaphragm is that

this provides no means for properly centering the diaphragm between the anode and the cathode at the optimum point of voltage so as to obtain maximum production. Even without shaking the collector-diaphragm the diaphragm may become displaced from the optimum voltage point due to uneven expansion of cell parts or other operational incidents.

It is therefore an object of the present invention to improve the fused salt sodium cell so that production will be more efficient and operation safer. It is a more specific object to design the cell so that the diaphragm may be shaken independently of the collector system. Another object is to provide for centering the diaphragm in the cell at the position for optimum production.

These and other objects are accomplished according to the present invention as described in detail hereafter.

I have discovered that the diaphragm can be so attached to the collector assembly in the Downs type cell that it can be moved or gently shaken horizontally between the anode and the cathode without interrupting the electrolysis process or without contacting anode or cathode and that then the diaphragm can be positioned at the point of maximum voltage between anode and cathode. By thus "shaking" the diaphragm and positioning it at the optimum voltage point it is possible to dislodge solid impurities that lodge between the diaphragm and the cathode and thus to achieve optimum production of sodium from the cell with very few diaphragm replacements required during the entire life of the cell.

My invention is further illustrated by the drawings of which Figure 1 is a vertical cross section of a four-anode sodium cell. The upper part of the figure from A—A is a cross section through the vertical center of the cell below A—A the cross section is through the center line of two anodes with cathodes, diaphragms and collector system exposed.

Figure 2 is a horizontal schematic section of the cell of Figure 1 at C—C showing the collector rings.

Figure 3 is a horizontal schematic section of the cell of Figure 1 at B—B through the diaphragm rings.

The reference numerals refer to the same parts in all the figures of the drawing. The cell proper is contained within the insulating lining 1 which holds the fused salt bath with a level as at 2. The anodes 4 are supported in metal housing 3 which makes electrical contact with bus bar 5. Cathode 6 surrounds each anode 4 at a distance usually not over three inches and makes electrical contact by way of cathode arms 7 and bus bars 8. Diaphragms 9 are cylindrical and are interposed between each anode and its encircled cathode. The diaphragm is usually made of closely woven iron or steel wire mesh and is integrally fastened to diaphragm ring 10 which imparts form and rigidity to the diaphragm. Each diaphragm ring by way of lug 15 is supported on horizontally slidable bar 11 and by way of diaphragm pivot lug 12 is attached by means of a pivot pin 14 which engages with a lug 12′ fastened integrally to chlorine collector 18. The lugs 12 and 12′ are superposed vertically to engage pivot pin 14. The slidable bar 11 is supported on stationary bar 16 which in turn is attached by hanger braces 17 to the chlorine collectors 18 by way of tie rod 17′. The chlorine collectors 18 are an integral part of the collector system which also comprises the chlorine collector dome 19 and the sodium collector 20 and associated sodium riser pipe 21. With handle rod or bar 22 by way of pinion 23 a reversible sliding action can be imparted to slidable bar 11 and thereby the diaphragm 9 can be moved back and forth within the limits of the space between the electrodes. Movement from the slidable bar 11 is imparted to the diaphragm rings 10 by

means of pivot 24 which engages the lugs 15 which are cut as shown to permit limited lateral movement. A volt meter 25 is connected between bus bars 5 and 8 to indicate the voltage drop through the cell.

During electrolysis conductive solids tend to accumulate at some place between the cathode 6 and the diaphragm 9. This accumulation is of a pasty character since the solids as produced are finely divided and surrounded by molten cell bath. However, given more or less time these solids will agglomerate and grow in size until they form an electric short circuit between the diaphragm and the cathode. Now, it has been discovered that if the diaphragm is moved gently laterally before the agglomerated mass consolidates or hardens the solids can be easily dislodged by contact with the diaphragm and induced circulation due to movement of the diaphragm while shaking and they then either drop to the bottom of the cell or are dispersed in the cell bath by the naturally occurring circulation of the bath which may be due to various causes such as temperature induced variations in density, convection currents, the lifting effect of the rising chlorine and sodium and others. Such dispersed solids may in part react with the cell bath to form bath soluble components or may eventually settle to the bottom of the electrolyte.

According to my invention the diaphragm in the cell is moved laterally backwards and forwards by engaging the diaphragm ring at the top of the diaphragm in such a way that the entire diaphragm moves only horizontally without vertical distortion. The ring is pivoted at a point opposite the engaging point. This back-and-forth movement actually constitutes a shaking operations during which the deposition of solids between the cathode and the diaphragm is disrupted and the solids are "shaken" or washed loose. If this operation is performed at suitable periodic intervals, as indicated by cell voltage and then shaken and positioned for periods such as every thirty or sixty minutes, it has been found that no electrical shorts will develop during many days of continuous cell operation.

It was also discovered that the voltage between the anode and the cathode varies with the position of the diaphragm. As the diaphragm approaches either electrode the voltage drops. The voltage goes through a maximum point at approximately the middle position of the diaphragm between the electrodes. Observation of cell operation over extended periods has lead to the discovery that production of sodium and chlorine is at a maximum if the diaphragm is placed at the position of highest indicated voltage reading as it is moved back and forth or "shaken" after completing this operation and left at this point until the next shaking operation. Accordingly after the diaphragm is shaken it is returned to the optimum or highest voltage position and secured there during the interval between shakings.

Each shaking operation requires at least one forward and backword movement of the shaker arm. Generally 3 to 10 such movements are adequate.

My invention is not limited to the multiple anode fused salt electrolysis cell which has been used to exemplify the principles of shaking the diaphragm horizontally within the space between the anode and the cathode to dislodge accumulating solids and then positioning the diaphragm at the optimum voltage point between the electrodes but it may be used in single anode cells as well or in cells having any desired number of anodes.

The diaphragm as described in detail is supported on two points, namely the pivot 14 and lug 15 at which latter point the diaphragm is engaged for shaking and for positioning of the diaphragm at optimum voltage by slidable bar 11. However, the diaphragm may be supported at more than two points and it may be shaken at more than one point as will be evident to those skilled in the art, provided that the supports permit movement of the diaphragm laterally, i.e., horizontally only and provided the diaphragm may be positioned at the optimum voltage point between the electrodes during electrolysis between the shaking operations.

It is also essential for the success of my invention that the diaphragm be firmly fixed to a member, such as a heavy ring, in the zone above the electrolysis zone between the electrodes which member will impart rigidity or stiffness to the diaphragm. Further, without such a member the diaphragm could not be supported so as to permit easy shaking. Also, this member preferably constitutes the means for supporting the weight of the diaphragm in horizontally slidable disposition while keeping the diaphragm in substantially vertical alignment between the electrodes and without any part thereof making direct electrical contact with either electrode.

The diaphragm may be "shaken" manually be means of handle 22 as shown or the shaking operation may be performed by automatic means set to function periodically at predetermined intervals such as 30 minutes. Preferably the automatic shaking will be occasioned by an automatic continuous reading instrument which will function without manual intervention whenever the voltage reading at 25 varies from the optimum by a reading of about 0.1 to 0.2 volts and will then maintain the diaphragm at the optimum position during electrolysis. Such means for automatic actuation based on voltage change are readily available or adaptable by those skilled in the art and therefore require no further detailed description here.

I claim:

1. In a fused salt cell for the production of alkali metal and halogen the combination comprising a submerged cylindrical vertically disposed anode, an annular cathode surrounding said anode at a distance not greater than about three inches, a cylindrical diaphragm disposed vertically in the space between the electrodes, said diaphragm being slidably supported above said electrodes to permit horizontal movement of the diaphragm within the space between said electrodes.

2. In a cell for the production of sodium and chlorine by the electrolysis of fused salt comprising a submerged vertical cylindrical anode, a spaced cylindrical cathode around said anode and, a cylindrical diaphragm interposed between said anode and said cathode, said diaphragm being integrally attached at its upper end to a diaphragm ring which in turn rests upon supports whereon said diaphragm ring is slidable over a horizontal distance smaller than the spaced distance between said anode and said cathode.

3. In a cell for the production of sodium and chlorine by the electrolysis of fused salt comprising a submerged vertical cylindrical anode, a spaced cylindrical cathode around said anode, a cylindrical diaphragm interposed between said anode and said cathode, said diaphragm being integrally attached at its upper end to a diaphragm ring which in turn rests upon supports whereon said diaphragm ring is slidable over a horizontal distance smaller than the spaced distance between said anode and said cathode, and means for positioning the diaphragm between the electrodes at the point of greatest voltage drop between said electrodes.

4. In a cell for the production of sodium and chlorine by the electrolysis of fused salt comprising a submerged vertical cylindrical anode, a spaced cylindrical cathode around said anode, a cylindrical diaphragm interposed between said anode and said cathode, said diaphragm being integrally attached at its upper end to a diaphragm ring which in turn rests upon supports whereon said diaphragm ring is slidable over a horizontal distance smaller than the spaced distance between said anode and said cathode, and means for actuating the slidable movement of said diaphragm whenever there is a change in the voltage between the anode and the cathode.

5. In the operation of a fused salt electrolysis cell provided with an annular vertically disposed anode, a cathode encircling said anode at a distance of less than than three inches and a porous diaphragm between said anode and cathode, the steps comprising passing an electric current between the electrodes to generate sodium and chlorine and shaking said diaphragm by moving it horizontally within the space between said electrodes without contacting said electrodes and while maintaining said electric current, and then positioning said diaphragm at the point of maximum voltage between said electrodes until the next period of shaking the diaphragm and repeating the process periodically.

6. In the operation of a fused salt electrolysis cell provided with an annular vertically disposed anode, a cathode encircling said anode at a distance of less than three inches and a porous diaphragm between said anode and

cathode, the steps comprising passing an electric current between the electrodes to generate sodium and chlorine, shaking said diaphragm horizontally within the space between said electrodes without contacting either electrode, said shaking being performed whenever the voltage between said electrodes varies from the optimum by more than about 0.1 volt, then positioning said diaphragm at the point of maximum voltage between said electrodes until there is a voltage change and then repeating the shaking operation and positioning of the diaphragm at the point of optimum voltage.

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