United States Patent Office

3,505,200
Patented Apr. 7, 1970



3,505,200

# ANTHOPHYLLITE ASBESTOS DIAPHRAGM FOR CHLOR-ALKALI ELECTROLYTIC CELLS

Morris P. Grotheer, Lewiston, N.Y., assignor to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

No Drawing. Filed Dec. 1, 1966, Ser. No. 598,165
Int. Cl. B01k 3/10
U.S. Cl. 204—295 4 Claims

## ABSTRACT OF THE DISCLOSURE

Anthophyllite asbestos for chlor-alkali high density electrolytic cells.

This invention relates to an improved asbestos diaphragm composition particularly suited for use in chlor-alkali diaphragm cells. In addition, this invention relates to a method of controlling the cell-liquor caustic concentration in chlor-alkali diaphragm cells by selection of a diaphragm composition which provides the desired diaphragm porosity.

Asbestos diaphragms have been used for many years in chlor-alkali cells. Chrysotile asbestos has been the type of asbestos almost exclusively used for chlor-alkali cell diaphragms. Various other types of fibrous asbestos are also known and used. While chrysotile asbestos provides desirable properties with respect to voltage drop and general serviceability, it has been found to have the disadvantage of providing only a relatively narrow range of porosities when deposited on a foraminous cathode of an electrolytic cell. Changes in the weight or thickness of the applied asbestos, and/or the fiber length only slightly change the porosity characteristics. Thus, in commercial cell operations, the caustic strength is limited, under normal operating conditions, to about 120 to 160 grams per liter of caustic and with normal cell liquor concentrations being about 140 grams per liter of caustic. This concentration cannot normally be greatly varied, especially in a manner whereby a lower caustic concentration can be achieved without changing the operation of the cell.

There are improvements in chlor-alkali diaphragm cell operations wherein it is desirable to acidify the anolyte feed solution. This type of operation can result in the tightening or restriction of the electrolyte flow through the diaphragm due to changes in the porosity of the diaphragm. A slower flow through the diaphragm increases the concentration of caustic in the produced cell liquor. In many respects this is undesirable particularly because increased caustic strengths can adversely affect the anode current efficiency as well as adversely affect the salt-caustic ratio which in turn affects the current efficiency. Also, because of the limited porosity variance, high current density cells were impractical.

It is an object of the present invention to provide an asbestos composition of greater acid resistance particularly suited for use with chlor-alkali diaphragm cells. It is another object of the present invention to provide an asbestos composition which can be regulated to provide the desired porosity for any chlor-alkali electrolysis and which can be used to regulate the flow characteristics through the diaphragm to produce a cell liquor of any chosen caustic concentration. A further object of this invention is to provide a diaphragm of increased electrolyte porosity, low gas permeability and low resistance, particularly suited for use with high current density chlor-alkali cells. These and other objects will become apparent to those skilled in the art from the description of the invention which follows.



In accordance with the invention, an asbestos diaphragm composition is provided for an electrolytic cell comprising a mixture of fibrous asbestos comprising about 5 to 95 percent weight of anthophyllite. In accordance with a further embodiment of the invention, a method of operating a chlor-alkali diaphragm cell having an anode and a cathode separated by a porous diaphragm into an anolyte compartment and a catholyte compartment is provided comprising forming a diaphragm between said anode and a cathode, said diaphragm comprising an anthophyllite asbestos composition, imposing a decomposition voltage between said anode and cathode, and passing an aqueous chloride containing electrolyte from said anolyte compartment through said diaphragm to said catholyte compartment thereby partially electrolying said chloride in said solution to produce chlorine, hydrogen and a caustic containing electrolyte.

The present invention is particularly useful with chlor-alkali cells employing various improved methods of operating chlor-alkali diaphragm cells. In particular, methods utilizing acid additions to the anolyte compartment are greatly benefitted by the present invention because the flow characteristics through the present diaphragm can be more closely controlled with less of the previously encountered "tightening" of the diaphragm and lessening of the porosity thereof on acidification of the anode electrolyte. Also, the present diaphragm is particularly useful in high current density cells wherein the flow rates through previous diaphragms with comparable gas permeabilities and voltage drops is too slow to maintain high current efficiencies due to the undesirable salt-caustic ratios. Further, the present invention is particularly useful wherein a chlor-alkali diaphragm cell is utilized to produce chlorates. Under such methods, it is often desirable to maintain a relatively high concentration of chlorate in the feed liquor and to control the electrolysis of the chloride to produce a more desirable reaction solution for the production of further chlorates. Thus, depending upon the porosity desired, the diaphragm composition can be custom blended to provide porosity particularly suited for a given electrolytic process.

There are several known osbestos materials. Each of these materials has certain specific characteristics and various chemical resistances. Chrysotile has for many years been used as the asbestos material for chlor-alkali diaphragm cells. Chrysotile has a theoretical formula of $3MgO \cdot 2SiO_2 \cdot 2H_2O$. Another asbestos, crocidolite, is also suitable for chlor-alkali diaphragm cell use. It has a theoretical chemical formula of $NaFe(SiO_3)_2 \cdot FeSiO_3 \cdot XH_2O$. The asbestos used in the present invention to provide the asbestos compositions in accordance with the present invention is anthophyllite having a theoretical formula of $(MgFe)_7Si_8O_{22}(OH)_2$.

Anthophyllite differs from previously used diaphragm asbestos, particularly in its acid resistance and high porosity. The asbestos for diaphragm use is preferably of a fibrous nature which lends itself to depositing from an aqueous solution onto a foraminous cathode. However, the asbestos can be also utilized in paper or fabric form and applied as such to the cathode. However, the fibrous compositions wherein the asbestos is of either a mixture of fiber lengths or of substantially the same length are preferred. The diaphragm is made by forming the asbestos, usually by applying to a foraminous cathode, into a liquid permeable membrane of about 0.1 to about 1 pound asbestos per square foot and more preferably, about 0.2 to 0.5 pound asbestos per square foot.

In comparison to the previously used chrysotile asbestos, anthophyllite is about 5 times more permeable at


Published by AsbestosClaims.Law
asbestosclaims.law/library/21668/1

equal diaphragm weights and hydrostatic pressures and about 6 times more acid resistant than chrysotile. It has been discovered that by blending the anthophyllite with another asbestos, particularly chrysotile, a very wide range of porosities and acid resistances can be obtained. As an indication of the porosity range, the flow through a 0.3 pound per square foot diaphragm can be varied from a flow rate of about 1850 cubic centimeters per minute per square foot of diaphragm area at a constant hydrostatic pressure of about 10 inches with 100 percent anthophyllite to about 30 cubic centimeters per minute per square foot of diaphragm area with mixtures of anthophyllite and chrysotile approaching 100 per cent chrysotile. Somewhat greater and lesser flow rates can be obtained by varying the diaphragm weight. Preferably, between about 5 to 95 per cent anthophyllite is used with another asbestos, particularly chrysotile, to obtain the particular permeability desired. Although chrysotile is preferred as the second asbestos, other asbestos can be used with correspondingly good results.

The particular amount of anthophyllite utilized is determined by the particular type of cell operation contemplated, the anolyte acidity to be employed and the desired caustic concentration in the cell liquor produced. With greater percentages of anthophyllite, using the same electrical currents, a more acid resistant diaphragm is obtained and a lower concentration of caustic in the cell liquor is also obtained at the same hydrostatic pressure. If high acid resistance is desired without greatly reducing the caustic strength, higher diaphragm weights are employed. By utilizing a more acidic anolyte, such as in the range of a pH of about 1 to 4, graphite consumption is reduced and higher anode current efficiencies are obtained. In the same manner, with controlled caustic concentrations, improved salt-caustic ratios can be obtained in the catholyte with correspondingly improved anode current efficiencies.

The present diaphragms are particularly useful for the electrolysis of a chloride containing solution. The chloride containing solutions are alkali metal chloride solutions. These include chlorides having a cation of sodium, potassium, lithium, rubidium, cesium, and the like. The caustic produced by the electrolysis is the corresponding hydroxyl of the cation employed. Therefore, caustic is used herein in its generic sense to denote an alkali metal commensurate with the chloride cation used.

In the process of this invention, a caustic concentration in the range of about two grams per liter, up to about 180 grams per liter at a normal current density of about 0.7 to 0.9 amperes per square inch can be readily obtained. With correspondingly greater and lesser current densities a correspondingly increase or decrease in caustic concentration is obtained as will be readily recognized by those skilled in the art. The lower caustic concentrations such as about 20 to 80 are particularly desirable when the produced cell liquor is utilized for the production of chlorates by reaction with chlorine. Under such conditions, the particular strength of the cell liquor (catholyte liquor) is of lesser importance than when the cell liquor is to be converted to a concentrated caustic solution. However, when used for chlorate manufacture, the lower caustic concentration enhances current efficiency and, therefore, is particularly desirable especially when high concentrations of sodium chlorate are also present in the cell liquor. Thus, under a preferred chlorate method of operation, a cell liquor of a concentration of about 20 to 80 grams per liter of caustic is produced using a diaphragm weight of about 0.10 to 0.40 pounds per square foot of cathode area and an asbestos composition of about 30 to 70 percent by weight of anthophyllite, the remaining percentages being chrysotile.

The favorable characteristics of anthophyllite makes high current density chlor-alkali diaphragm cells practical because the caustic concentration can now be controlled to provide the most favorable range of salt-caustic ratios in the catholyte thereby retaining high current efficiencies. Previous diaphragm cells did not operate favorably at current densities above about 1.0 ampere per square inch of cathode surface. Using the present diaphragm composition, high current densities of 1 to about 5 amperes per square inch of cathode surface and more preferably, about 1 to about 2.5 amperes per square inch of cathode surface as well as at the previous lower current densities can be used while maintaining favorable salt-caustic ratios and current efficiencies. For instance, at any of the high current densities stated, a catholyte liquor having a caustic concentration in the range of about 2 to 180 grams per liter of caustic and more preferably for chlorine caustic production about 130 to 155 grams per liter of caustic can be obtained by selecting the anthophyllite composition and weight thereof to provide the desired porosity.

The chloride solution electrolyzed is preferably of a concentration of about 120 to 330 grams per liter of chloride material. Concentrations near saturation are preferred. When a chlorate is also present in the solution to be electrolyzed, the chloride concentration is correspondingly reduced so that when sodium is the cation at a chlorate concentration of about 650 grams per liter, the chloride concentration, at about 85 degrees centigrade, is near saturation at about 120 grams per liter of NaCl. Thus, the chlorate concentration in the feed solution can be varied from 0 to about 600 grams per liter. When the present process is used to make caustic, it is preferred to use a feed solution comprised primarily of chloride at a concentration of about 260 to 330 grams per liter. When the present process is to be used for the production of chlorates, the feed solution preferably comprises 300 to 650 grams per liter of chlorate and about 120 to 230 grams per liter of chloride.

In the following examples, sodium chloride is used as the chloride because of its greater commercial utility. However, it is to be noted that other alkali metal chlorides can be used with correspondingly good results. Therefore, in referring to sodium chloride, it is to be considered that other alkali metal chlorides can also be used in the same manner.

The following examples illustrate certain embodiments of the present invention. Unless otherwise indicated, all parts and percentages used herein are by weight and all temperatures in the examples and claims are in degrees centigrade.

## EXAMPLES 1–8

These examples illustrate a method in accordance with the invention of operating a chlor-alkali diaphragm cell of a specified asbestoes composition in a manner particularly suited for the production of a cell liquor for reaction with chlorine to produce sodium chlorate. In this method of operation the chlorate concentration is maintained at a relatively high level so that a crop of chlorate crystals can be readily removed without an excessive evaporation or greatly varying the electrolyte temperature.

The asbestos diaphragn was deposited on a foraminous steel cathode in the desired amount as noted in the examples from a water dispersion of the asbestos by the application of suction. The electrolytic cell was assembled with the porous diaphragm separating the anode and the cathode into an anolyte compartment and a catholyte compartment. The cell was operated by feeding the stated solution of sodium chloride to the anolyte compartment wherein it was electrolyzed to produce chlorine. The solution was passed through the diaphragm to the catholyte compartment wherein it was further electrolyzed to produce hydrogen and caustic soda. In each of the following examples, the hydrostatic pressure applied to the solution at the diaphragm was substantially the same. The electrolysis was effected at a current density of 0.834 ampere per square inch of cathode and a temperature of 80 degrees centigrade. The results obtained are shown in Table I.

TABLE I

| Example No. | Diaphragm Weight [1] | Flow rate through diaphragm [2] | Anolyte Composition in grams per liter | | | Catholyte Composition in grams per liter | | | Current efficiency |
|---|---|---|---|---|---|---|---|---|---|
| | | | NaCl | $NaClO_3$ | pH | NaCl | $NaClO_3$ | NaOH | |
| 1. 100% Anthophyllite | 0.30 | 1,850 | 136 | 574 | 3.0 | 135 | 582 | 2 | ---- |
| 2. 100% Anthophyllite | 0.60 | 475 | 135 | 618 | 2.7 | 128 | 618 | 7.8 | 98.3 |
| 3. 100% Anthophyllite | 0.60 | 420 | 128 | 596 | 2.8 | 120 | 568 | 8.8 | 97.2 |
| 4. {66% Chrysotile / 33% Anthophyllite} | 0.30 | 44 | 130 | 606 | 2.0 | 99 | 558 | 84.0 | 99.0 |
| 5. {33% Chrysotile / 66% Anthophyllite} | 0.30 | 340 | 129 | 592 | 2.7 | 123 | 580 | 11.0 | 97.8 |
| 6. {40% Chrysotile / 60% Anthophyllite} | 0.30 | 102 | 128 | 590 | 2.5 | 123 | 580 | 36.4 | 98.3 |
| 7. 55% Chrysotile | 0.30 | 55 | 128 | 574 | 2.5 | 120 | 526 | 68 | 98.0 |
| 8. 100% Chrysotile | 0.30 | 26.5 | 270 | ---- | 3.0 | 170 | ---- | 140 | 96.0 |

[1] Pounds per square foot of cathode.
[2] Cubic centimeters per min. per square foot at 10 in. hydrostatic head.

In the above examples it will be readily seen that the rate of electrolyte through the diaphragm can be readily controlled to provide the desired concentration of caustic in the catholyte liquor while providing high current efficiencies.

In the same manner, the present invention can be operated at higher sodium chloride concertation of about 230 to 330 grams per liter without the presence of sodium chlorate with correspondingly good results. Also, in place of sodium chloride, potassium chloride, lithium chloride, cesium chloride, and rubidium chloride are used as the chloride feed material with correspondingly good results.

## EXAMPLES 9–14

A chlor-alkali cell is operated using the various diaphragn compositions in this invention to produce chlorine, hydrogen and caustic soda using a variable brine feed commensurate with a constant hydrostatic heat and an acidified brine of a feed concentration of 325 grams per liter of sodium chloride and an anolyte jH of about 3. foot of cathode surface. Caustic soda concentrations above about 160 grams per liter are not economically obtained without special operating procedures and therefore, such cell liquor of the noted caustic concentration is produced at the noted current densities given in amperes per square Using the various anthophyllite compositions, a catholyte higher concentrations have not been shown. Example 9 represents the prior art asbestos diaphragn.

TABLE II

| Example Number | Percent by weight of Anthophyllite | Percent by weight of Chrysotile | Cell liquor concentration if NaOH in grams per liter at noted amperage in amperes per square foot of cathode surface | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 125 | 150 | 200 | 250 | 300 | 350 |
| 9 | 0 | 100 | 140 | ---- | ---- | ---- | ---- | ---- |
| 10 | 10 | 90 | 116 | 139 | ---- | ---- | ---- | ---- |
| 11 | 25 | 75 | 95 | 114 | 152 | ---- | ---- | ---- |
| 12 | 50 | 50 | 75 | 90 | 120 | 150 | ---- | ---- |
| 13 | 75 | 25 | 59 | 71 | 94 | 118 | 141 | ---- |
| 14 | 100 | 0 | 23 | 28 | 37 | 46 | 55 | 64 |

While there have been described various embodiments of the present invention, the compositions and methods described are not intended to limit the scope of the invention as it is realized that changes therein are possible. It is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner. It is intended to cover the invention broadly in whatever form its principles may be utilized.

What is claimed is:

**1.** An electrolytic cell comprising a container housing an anode and a cathode separated by a diaphragm, said diaphragm comprising anthophyllite asbestos.

**2.** The electrolytic cell of claim **1** wherein the asbestos diaphragn composition comprises about 5 to 95 percent by weight of anthophyllite.

**3.** The electrolytic cell of claim **1** wherein the asbestos mixture contains chrysotile.

**4.** The electrolytic cell of claim **1** comprising 30 to 70 percent anthophyllite with the remaining percentages being substantially chrysotile.

### References Cited

Ladoo, Non-Metallic Minerals, 1st Ed., 1925, p. 43, McGraw-Hill Book Co.

Electrochemical Society Preprint 67–20, Mar. 25, 1935, pp. 265, 273–284.

JOHN H. MACK, Primary Examiner

S. S. KANTER, Assistant Examiner

U.S. Cl. X.R.

204—266



Published by AsbestosClaims.Law

asbestosclaims.law/library/21668/3

PO-1050
(5/69)

# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,505,200 Dated April 7, 1970

Inventor(s) Morris P. Grotheer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 15, delete "electrolying" and insert -- electrolyzing --; Column 2, line 42, delete "osbestos" and insert -- asbestos --; Column 4, line 50, delete "asbestoes" and insert -- asbestos --; Column 4, line 58, delete "diaphragn" and insert -- diaphragm --; Column 5, line 33, delete "diaphragn" and insert -- diaphragm --; Column 5 line 37 delete "jH" and insert -- pH --; Column 5, line 38, delete "foot of cathode surface" and insert -- Using the various anthophyllite compositions, a catholyte cell liquor of the noted caustic concentration is produced at the noted current densities given in amperes per square foot of cathode surface --; Column 5, lines 41-43, delete in their entirety. Column 5, line 45, delete "diaphragn" and insert -- diaphragm --; Claim 2, line 2, delete "diaphragn" and insert -- diaphragm --.

SIGNED AND
SEALED
AUG 18 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents