United States Patent [19]

Cook, Jr.

[11] **3,897,320**

[45] **July 29, 1975**

[54] **ELECTROLYTIC MANUFACTURE OF CHLORATES, USING A PLURALITY OF ELECTROLYTIC CELLS**

[75] Inventor: **Edward H. Cook, Jr.**, Lewiston, N.Y.

[73] Assignee: **Hooker Chemicals & Plastics Corporation**, Niagara Falls, N.Y.

[22] Filed: **Nov. 1, 1973**

[21] Appl. No.: **411,622**

[52] **U.S. Cl.** **204/95**; 204/98; 204/257; 204/128; 204/263

[51] **Int. Cl.** **C01b 11/26**; C01d 1/06; B01k 3/00

[58] **Field of Search** 204/95, 98

[56] **References Cited**

UNITED STATES PATENTS

665,426	1/1901	Gibbs	204/95
2,584,824	2/1952	Vanharen et al.	204/95
3,234,110	2/1966	Beer	204/290 F
3,438,879	4/1969	Kircher et al.	204/95
3,535,215	10/1970	Grotheer	204/95
3,657,102	4/1972	Keith et al.	204/290 F
3,784,399	1/1974	Grot	260/79.3 MU

FOREIGN PATENTS OR APPLICATIONS

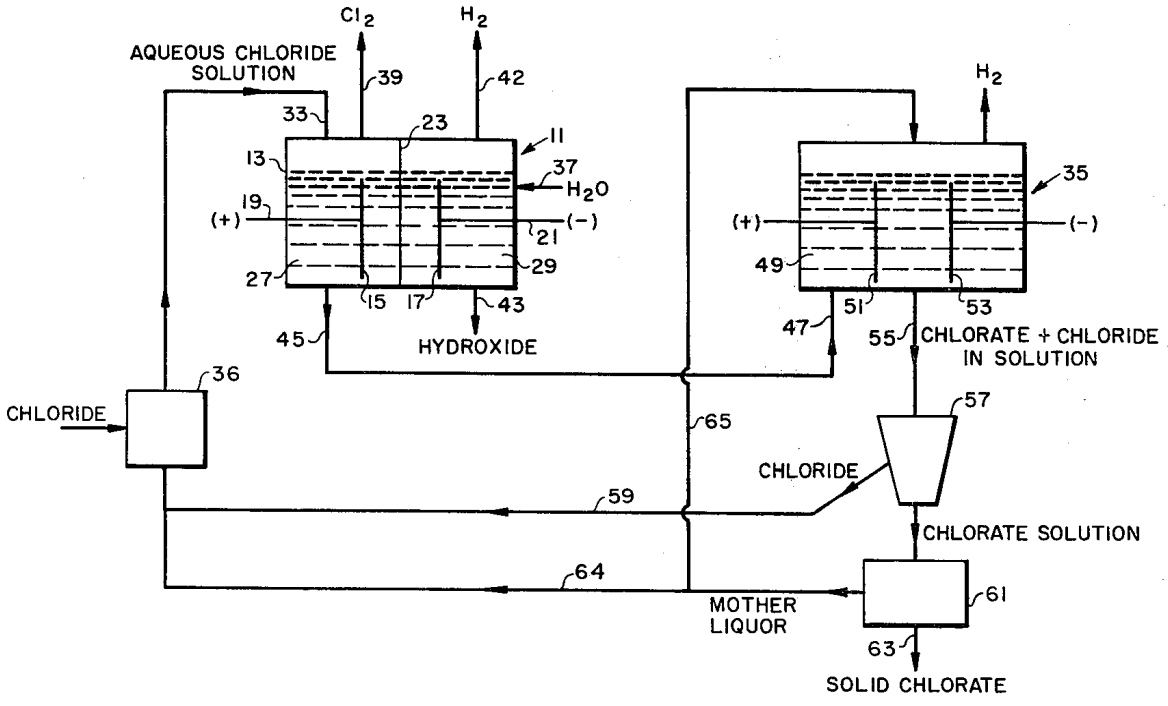
1,045,675	10/1966	United Kingdom	204/92

Primary Examiner—F. C. Edmundson
Attorney, Agent, or Firm—Peter F. Casella

[57] **ABSTRACT**

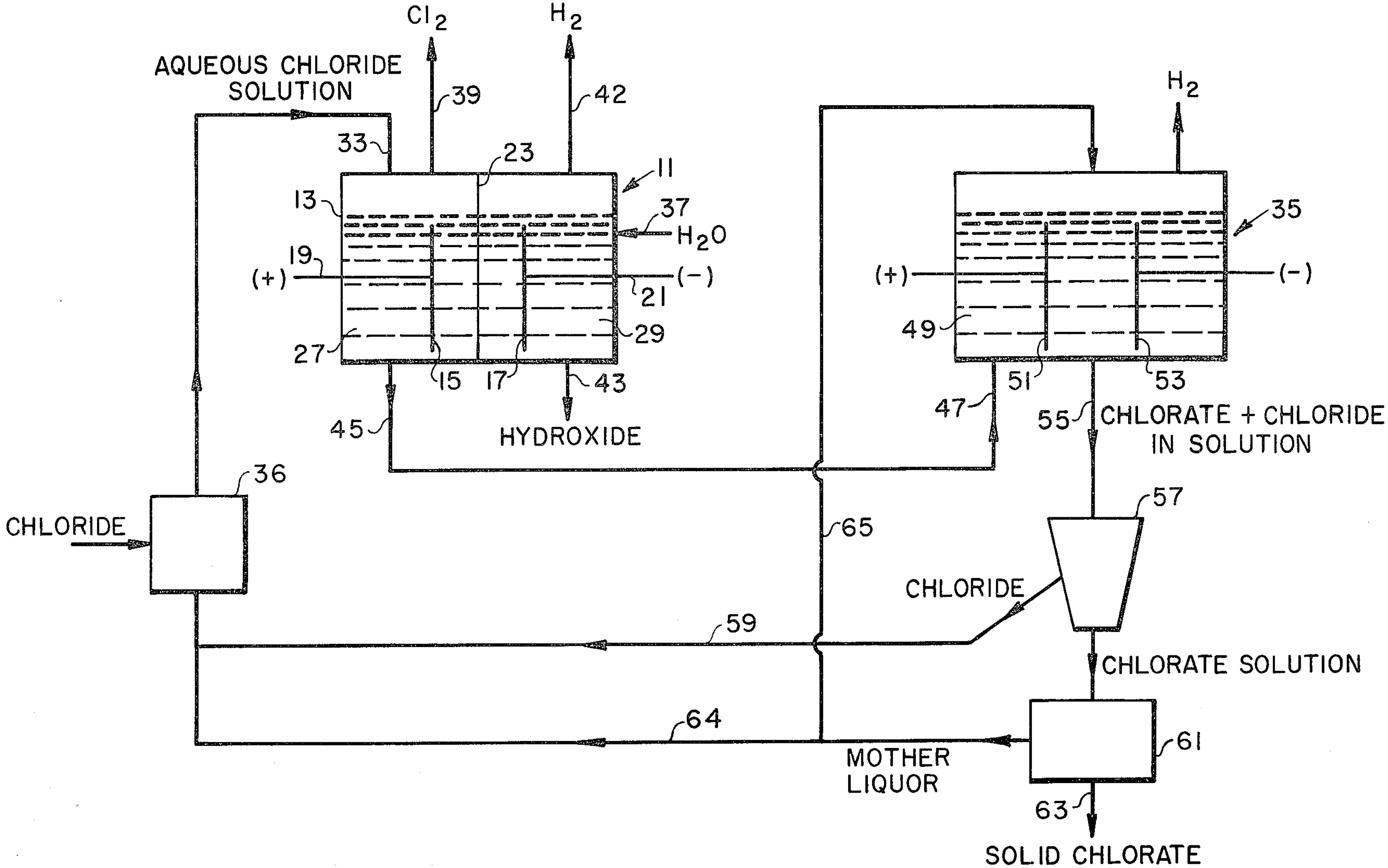
A sodium chloride solution is electrolyzed to produce a high strength caustic solution and sodium chlorate solution, using two different electrolytic cells. In the first cell, a two-compartment cell in which the compartments are separated by a permselective membrane of a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether or of a sulfostyrenated perfluorinated ethylene propylene polymer, the sodium chloride solution is electrolyzed at a pH of about 4 to 7 to produce aqueous sodium hydroxide solution in the cathode compartment and chlorine and cell liquor containing chlorate in the anode compartment. Then, the cell liquor, already containing some chlorate, is further electrolyzed in a conventional chlorate cell or equivalent apparatus to convert chloride therein to chlorate. After separation of the chlorate from chloride present with it the chloride is returned to the first cell.

6 Claims, 1 Drawing Figure



PATENTED JUL 29 1975

3,897,320



ELECTROLYTIC MANUFACTURE OF CHLORATES, USING A PLURALITY OF ELECTROLYTIC CELLS

This invention relates to the electrolytic manufacture of chlorates. More specifically, it is of a process for making alkali metal chlorate, alkali metal hydroxide, chlorine and hydrogen from aqueous alkali metal chloride solution by electrolysis of the solution in a two compartment cell equipped with an effective cation-active permselective membrane divider, with the production of some chlorate in the anolyte, and subsequent electrolysis of the anolyte in a chlorate cell. Polymeric material found to be effective as the membrane is a hydrolyzed polymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether or is a sulfostyrenated perfluorinated ethylene propylene polymer.

An advantage of this invention is that alkali metal chlorate produced by transmission of hydroxide through the membrane into the anolyte is recovered and the "contaminated" (chlorate-containing) anolyte is subsequently utilized as a feed to a chlorate cell. Satisfactory efficiencies are obtained under the process conditions and little or no hydrochloric acid is needed for the treatment of the anolyte.

In accordance with the present invention a method for electrolytically manufacturing hydroxide, chlorine and chlorate comprises electrolyzing an aqueous solution containing chloride ions in an electrolytic chlorine cell having anode and cathode compartments, an anode, a cathode, a cation-active permselective membrane of a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether, or of a sulfostyrenated perfluorinated ethylene propylene polymer, defining a boundary between the cathode and anode compartments and between the anode and the cathode, to produce an aqueous hydroxide solution and hydrogen in the cathode compartment and chlorine and chlorate in the anode compartment, removing the aqueous hydroxide solution and anolyte liquor containing chlorate and further electrolyzing the liquor in a chlorate cell to convert chloride therein to chlorate.

The invention will be readily understood by reference to the following descriptions of embodiments thereof, taken in conjunction with the drawing in which:

The FIGURE is a schematic representation of the arrangement of cells and equipment for producing chlorate with hydroxide, chlorine and hydrogen.

In the FIGURE electrolytic chlorine cell **11** includes outer wall **13**, anode **15**, cathode **17** and conductive means **19** and **21** for connecting the anode and the cathode to sources of positive and negative electrical potentials, respectively. Inside the walled cell cation-active permselective membrane **23** divides the volume into anode or anolyte compartment **27** and cathode or catholyte compartment **29**. Alkali metal halide solution is fed to the anolyte compartment through line **33** and chloride, separated out from chlorate-chloride solution produced in chlorate cell **35**, is employed to make up halide feed to the anode compartment, being added with other chloride to resaturator **36**. Water is fed to the cathode compartment **29** through line **37**. Of course, additions of electrolyte and water should be such as to maintain the desired liquid levels in the anode and cathode compartments and this may often be effected with feed-overflow devices and similar techniques, which are known in the art and therefore, are not illustrated.

In the present cell halogen, e.g., chlorine gas, is removable from the anolyte compartment through line **39** and hydrogen is removable from the catholyte compartment through line **42**. A comparatively high concentration of aqueous hydroxide solution may be taken off from the catholyte through exit **43**. Because the cation-active permselective membrane **23** allows some hydroxyl ions to migrate through it from the catholyte to the anolyte these can react to produce chlorate in the anolyte and the cell liquor resulting, a mixture of chlorate and chloride in aqueous solution, is removed at **45** and transferred through line **47** to the interior **49** of chlorate cell **35**. In such cell, due to the absence of any diaphragms or separators between anode **51** and cathode **53** the products of electrolysis, chlorine and hydroxide, interact and form chlorate, possibly also with the formation of some hypochlorite. By controlling the pH in the chlorate cell to be within the 6 to 7.5 range the production of chlorate can be favored. If desired, hypochlorite may be produced in the cell and converted externally to chlorate, which may then be processed further as described herein.

The chlorate and chloride in solution are removed from chlorate cell **35** through line **55** after the concentration of chlorate has increased sufficiently and that of chloride is low enough so as not to be salted out in the chlorate cell. Under the conditions employed the chloride is removed from the chlorate solution as a solid in separator **57** and then passes through line **59** or other suitable transfer mechanism to resaturator **36** and back to chlorine cell **11**. The chlorate is crystallized out of the solution in crystallizer **61**, being removed at **63**. The mother liquor remaining is sent back to the chlorine cell through line **64**, preferably via resaturator **36** or is recycled via line **65**.

The chlorine taken off from chlorine cell **11** may be burned in the hydrogen produced to form hydrochloric acid, which may be used to adjust pH in the resaturator, cell or separating and crystallizing apparatuses. Also, the chlorine may be reacted externally of the cell with hydroxide removed from the cell, to produce chlorate.

Various recirculations of compartment contents, preferably intracompartmentally, may also be employed. Although continuous processes such as illustrated are highly preferred, once-through processes, batch method and "hybrid" processes are also useful.

The main aspect of the present invention is in its utilization of a single permselective membrane chlorine cell to make high purity, high strength caustic solution and at the same time produce some chlorate in the anolyte, which is subsequently made useful by processing the anolyte liquor through a chlorate cell and recycling back to the chlorine cell non-chlorate products. It has been found that this process can be effected at anode efficiencies of over 85 percent and even over 90 percent and at caustic efficiencies over 75 percent and often over 80 percent.

The selective ion-passing effects of cationic membranes have been noted in the past but the membranes of this invention have not been employed in the present processes before and the unexpectedly beneficial effects resulting have not been previously obtained or suggested. Thus, with the use of a comparatively thin

membrane, preferably supported as described herein, several years of operation under commercial conditions are obtainable without the need for removal or replacement of the membrane, while all the time it efficiently prevents undesirable migration of chloride from the anode compartment to the cathode compartment, thus allowing production of high purity caustic. It prevents hydrogen formed on the cathode side from escaping into the halogen formed on the anode side and vice versa. In this respect the present membranes are superior to prior art membranes, being more impervious to the passage of gases, even when the membranes are very thin, than various other polymeric materials. The prevention of hydrogen mixing with chlorine is important since these materials form explosive mixtures, especially in the presence of oxygen, such as may be produced in the present processes. The superiority of the preferred membranes, including modified or surface treated versions thereof, over prior art membranes in the various described aspects is also evident, usually to a lesser degree, in the sulfostyrenated fluorinated ethylene propylene polymers.

The membranes employed are normally thin flat sheets, normally rectangular, but various other shapes and configurations may be employed. Plural membranes may be used together but usually this is of no special advantage. Buffer compartments may be formed but are detrimental to the carrying out of the present processes. Instead of monopolar electrodes, bipolar electrodes may be utilized.

The aqueous solution containing chloride ions is normally a water solution of sodium chloride, although potassium and other soluble chlorides, e.g., magnesium chloride, may be utilized, at least in part. However, it is preferred to employ the alkali metal chlorides and of these, sodium chloride is the best. Similarly, the chlorates made will preferably be alkali metal chlorates and the hydroxides will be alkali metal hydroxides, most preferably all being sodium compounds.

The concentration of sodium chloride in a charge to the anolyte and in the anolyte will usually be as high as feasible, normally being from 200 to 320 grams per liter for sodium chloride and from 200 to 360 g./l. for potassium chloride, with intermediates for mixtures thereof. The electrolyte may be acidified to a pH in the range of 2 to 6 but in many applications, as when hydrochloric acid is not readily available for acidification, instead of acidifying being to the range of 2 to 4, it may be to 4 to 7, preferably about 6, and may be that resulting from generation of chlorine in the anolyte and its neutralizaton, at least in part, by sodium hydroxide. A most preferred concentration of sodium chloride in water is 250 to 300 g./l. Because the chlorine cell anolyte, containing chlorate made therein, is the feed to the chlorate cell, the chloride content of the chlorate cell liquor is less than that of the chlorine cell anolyte fed to it, due to conversion of some of the chloride to chlorine and thence to chlorate in the chlorate cell. After removal of chloride and chlorate from the withdrawn chlorate cell liquor the chloride concentration will be still lower and the mother liquor which may be returned to the resaturator will normally be of less than 50 or 100 g./l. concentration. It may contain a smaller quantity of chlorate, too.

The presently preferred cation permselective membrane is of a hydrolyzed copolymer of perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether. The perfluorinated hydrocarbon is preferably tetrafluoroethylene, although other perfluorinated and saturated and unsaturated hydrocarbons of 2 to 5 carbon atoms may also be utilized, of which the monoolefinic hydrocarbons are preferred, especially those of 2 to 4 carbon atoms and most especially those of 2 to 3 carbon atoms, e.g., tetrafluoroethylene, hexafluoropropylene. The sulfonated perfluorovinyl ether which is most useful is that of the formula $FSO_2CF_2CF_2OCF(CF_3)CF_2OCF{=}CF_2$. Such a material, named as perfluoro[2-(2-fluorosulfonylethoxy)-propyl vinyl ether], referred to henceforth as PSEPVE, may be modified to equivalent monomers, as by modifying the internal perfluorosulfonylethoxy component to the corresponding propoxy component and by altering the propyl to ethyl or butyl, plus rearranging positions of substitution of the sulfonyl thereon and utilizing isomers of the perfluorolower alkyl groups, respectively. However, it is most preferred to employ PSEPVE.

The method of manufacture of the hydrolyzed copolymer is described in Example XVII of U.S. Pat. No. 3,282,875 and an alternative method is mentioned in Canadian Pat. No. 849,670, which also discloses the use of the finished membrane in fuel cells, characterized therein as electrochemical cells. The disclosures of such patents are hereby incorporated herein by reference. In short, the copolymer may be made by reacting PSEPVE or equivalent with tetrafluoroethylene or equivalent in desired proportions in water at elevated temperature and pressure for over an hour, after which time the mix is cooled. It separates into a lower perfluoroether layer and an upper layer of aqueeous medium with dispersed desired polymer. The molecular weight is indeterminate but the equivalent weight is about 900 to 1,600 preferably 1,100 to 1,400 and the percentage of PSEPVE or corresponding compound is about 10 to 30 percent, preferably 15 to 20 percent and most preferably about 17 percent. The unhydrolyzed copolymer may be compression molded at high temperature and pressure to produce sheets or membranes, which may vary in thickness from 0.02 to 0.5 mm. These are then further treated to hydrolyze pendant $-SO_2F$ groups to $-SO_3H$ groups, as by treating with 10 percent sulfuric acid or by the methods of the patents previously mentioned. The presence of the $-SO_3H$ groups may be verified by titration, as described in the Canadian patent. Additional details of various processing steps are described in Canadian Pat. 752,427 and U.S. Pat. No. 3,041,317, also hereby incorporated by reference.

Because it has been found that some expansion accompanies hydrolysis of the copolymer it is preferred to position the copolymer membrane after hydrolysis onto a frame or other support which will hold it in place in the electrolytic cell. Then it may be clamped or cemented in place and will be true, without sags. The membrane is preferably joined to the backing tetrafluoroethylene or other suitable filaments prior to hydrolysis, when it is still thermoplastic; and the film of copolymer covers each filament, penetrating into the spaces between them and even around behind them, thinning the films slightly in the process, where they cover the filaments.

The membrane described is far superior in the present processes to all other previously suggested membrane materials. It is more stable at elevated temperatures, e.g., above 75°C. It lasts for much longer time periods in the medium of the electrolyte and the caustic

product and does not become brittle when subjected to chlorine at high cell temperatures. Considering the savings in time and fabrication costs, the present membranes are more economical. The voltage drop through the membrane is acceptable and does not become inordinately high, as it does with many other membrane materials, when the caustic concentration in the cathode compartment increases to above about 200 g./l. of caustic. The selectivity of the membrane and its compatibility with the electrolyte do not decrease detrimentally as the hydroxyl concentration in the catholyte liquor increases, as has been noted with other membrane materials. Furthermore, the caustic efficiency of the electrolysis does not diminish as significantly as it does with other membranes when the hydroxyl ion concentration in the catholyte increases. Thus, these differences in the present process make it practicable, whereas previously described processes have not attained commercial acceptance. While the more preferred copolymers are those having equivalent weights of 900 to 1,600, with 1,100 to 1,400 being most preferred, some useful resinous membranes employable in present methods may be of equivalent weights from 500 to 4,000. The medium equivalent weight polymers are preferred because they are of satisfactory strength and stability, enable better selective ion exchange to take place and are of lower internal resistances, all of which are important to the present electrochemical cell.

Improved versions of the above-described copolymers may be made by chemical treatment of surfaces thereof, as by treatments to modify the $-SO_3H$ group thereon. For example, the sulfonic group may be altered on the membrane to produce a concentration gradient. Such a change may be made in the manufacturing process or after production of the membrane. When effected as a subsequent surface treatment of a membrane the depth of treatment will usually be from 0.001 to 0.01 mm. Caustic efficiencies of the invented processes, using such modified versions of the present improved membranes can increase about 3 to 20 percent, often about 5 to 15 percent. Exemplary of such treatments is that described in French patent publication 2,152,194 of March 26, 1973 in which one side of the membrane is treated with NH_3 to form SO_2NH_2 groups.

In addition to the copolymers previously discussed, including modifications thereof, it has been found that another type of membrane material is also superior to prior art films for applications in the present processes. Although it appears that tetrafluoroethylene (TFE) polymers which are sequentially styrenated and sulfonated are not useful for making satisfactory cation-active permselective membranes for use in the present electrolytic processes it has been established that perfluorinated ethylene propylene polymer (FEP) which is styrenated and sulfonated makes a useful membrane. Whereas useful lives of as much as three years or more (that of the preferred copolymers) may not be obtained, the sulfostyrenated FEP's are surprisingly resistant to hardening and otherwise failing in use under the present process conditions.

To manufacture the sulfostyrenated FEP membranes a standard FEP, such as manufactured by E. I. DuPont de Nemours & Co. Inc., is styrenated and the styrenated polymer is then sulfonated. A solution of styrene in methylene chloride or benzene at a suitable concentration in the range of about 10 to 20% is prepared and a sheet of FEP polymer having a thickness of about 0.02 to 0.5 mm., preferably 0.05 to 0.15 mm., is dipped into the solution. After removal it is subjected to radiation treatment, using a cobalt^{60} radiation source. The rate of application may be in the range of about 8,000 rads/hr. and a total radiation application is about 0.9 megarad. After rinsing with water the phenyl rings of the styrene portion of the polymer are monosulfonated, preferably in the paraposition, by treatment with chlorosulfonic acid, fuming sulfuric acid or SO_3. Preferably, chlorosulfonic acid in chloroform is utilized and the sulfonation is completed in about one-half hour.

Examples of useful membranes made by the described process are products of RAI Research Corporation, Hauppauge, New York, identified as 18ST12S and 16ST13S, the former being 18 percent styrenated and having two-thirds of the phenyl groups monosulfonated and the latter being 16 percent styrenated and having thirteen-sixteenths of the phenyl groups monosulfonated. To obtain 18 percent styrenation a solution of 17½ percent of styrene in methylene chloride is utilized and to obtain the 16 percent styrenation a solution of 16 percent of styrene in methylene chloride is employed.

The products resulting compare favorably with the preferred copolymers previously described, giving voltage drops of about 0.2 volt each in the present cells at a current density of 2 amperes/sq. in., the same as is obtained from the copolymer.

The membrane wall will normally be from 0.02 to 0.5 mm. thick, preferably from 0.1 to 0.5 mm. and most preferably 0.1 to 0.3 mm. When mounted on a polytetrafluoroethylene, asbestos, titanium or other suitable network, for support, the network filaments or fibers will usually have a thickness of 0.01 to 0.5 mm., preferably 0.05 to 0.15 mm., corresponding to up to the thickness of the membrane. Often it will be preferable for the fibers to be less than half the film thickness but filament thicknesses greater than that of the film may also be successfully employed, e.g., 1.1 to 5 times the film thickness. The networks, screens or cloths have an area percentage of openings therein from about 8 to 80 percent, preferably 10 to 70 percent and most preferably 30 to 70 percent. Generally the cross-sections of the filaments will be circular but other shapes, such as ellipses, squares and rectangles, are also useful. The supporting network is preferably a screen or cloth and although it may be cemented to the membrane it is preferred that it be fused to it by high temperature, high pressure compression before hydrolysis of the copolymer. Then, the membrane-network composite can be clamped or otherwise fastened in place in a holder or support.

The material of construction of the cell body may be conventional, including steel, concrete or stressed concrete lined with mastics, rubbers, e.g., neoprene, polyvinylidene chloride, FEP, chlorendic acid based polyester, polypropylene, polyvinyl chloride, TFE or other suitable plastic or may be similarly lined boxes of other structural materials. Substantially self-supporting structures, such as rigid polyvinyl chloride polyvinylidene chloride, polypropylene or phenol formaldehyde resins may be employed, preferably reinforced with molded-in fibers, cloths or webs.

The migration of caustic into the anolyte compartment of the chlorine cell may be controlled by regulat-

ing the concentration of caustic in the catholyte or by using a membrane of different thickness, more caustic being tranferred when the thickness is diminished. The rate of feed will determine to some extent the pH in the anolyte and it is desirable to keep this in the range of 3 to 7.5, preferably 3 or 4 to 7, so as to make chlorate. Recirculation rates may also be adjusted to help maintain the pH in the desired range and, as was mentioned previously, acids (or bases) may also be utilized. On the average it is considered that a controlled proportion, from 5 to 50 percent of the caustic produced in the catholyte compartment, as desired, may migrate to the anolyte compartment and the cell design and components may be varied to obtain the particular proportion most preferred. The pH of the chlorate cell may be regulated in similar manner.

In addition to controlling the pH's of the chlorine cell anolyte and the electrolyte of the chlorate cell the temperatures of these are also usually regulated. Normally they are maintained at less than 105°C., preferably being from 20° to **95**°C., more preferably from **50** to **95**°C. and most preferably about **60**° or **65**°C. to **85**° or **95**°C. Usually the chlorate cell is operated at about **70**°C. Electrolyte temperatures may be controlled by recirculation of various portions thereof or by changing the proportions of feed. When the temperature cannot be lowered sufficiently by reecirculation, refrigeration of the recirculating liquid(s) may also be utilized.

The processes of this invention, utilizing a single cation-active permselective diaphragm in a two compartment chlorine cell, operate at comparatively high efficiencies. By holding the anolyte pH in the range given, preferably at about 4.5, efficiencies of 80 percent (caustic efficiency) and more and of **90%** (anode efficiency) and more are obtainable. Under such conditions, **80%** caustic efficiency and 90 percent anode efficiency, two-compartment cells of the type described, rated at a capacity of 1 ton per day of chlorine, will produce about 0.9 T/d of sodium hydroxide, 0.8 T/d of chlorine and 0.05 T/d of sodium chlorate. The amount of chlorate produced will be increased, in accordance with the invention, by feeding the chlorine cell chlorate plus chloride into a chlorate cell. Of course, additional chloride may also be added to such cell.

The caustic made in the chlorine cell is free of chloride, normally containing as little as 0.1 to 10 g./l. thereof. Its concentration, which is usually from 250 to 450 g./l., may be increased by feeding dilute sodium hydroxide to the cathode compartment, recirculating sodium hydroxide solution previously taken off, increasing the electrolysis time or diminishing the rate of caustic takeoff. Alternatively, more concentrated solutions may be made by evaporation of the caustic produced. Of course, when more concentrated caustic is made in the catholyte the production of chlorate in the anolyte will be increased, since more caustic escapes to the anolyte and reacts.

The present cells lend themselves to use in both large and small plants, e.g., from 5 to 1,000 tons per day of chlorine or equivalent, based on the chlorine cells' production. In such cases the efficiencies described are obtainable so as to make the process economically desirable. It is highly preferred however, that the installation should be located near to and the product should be used in conjunction with a pulp bleaching plant, so that chlorate made can be employed as a bleach or in the production of a bleaching agent, e.g., chlorine dioxide, and the caustic may be employed in wood pulping operations.

The following examples illustrate but do not limit the invention. Unless otherwise indicated, all parts are by weight and all temperatures are in °C.

EXAMPLE 1

Employing the apparatus illustrated in the FIGURE, sodium chlorate, essentially chloride-free sodium hydroxide, chlorine and hydrogen are manufactured from an aqueous sodium chloride solution electrochemically, sequentially utilizing a chlorine cell and a chlorate cell. The chlorine cell is of asbestosfilled polypropylene, equipped with a dimensionally stable anode, and a steel cathode and the anode and cathode compartments of this two-compartment cell are separated by a cation-active permselective membrane. The single anode employed is of ruthenium oxide on titanium, with the titanium base being titanium mesh, 1 mm. in diameter, of about 50 percent open area, and the coating of ruthenium oxide being about 1 mm. thick. The anode is connected to a current source through titanium-clad copper rods. The steel cathode is of mild steel wire mesh, essentially **1** mm. in equivalent diameter, having about **35%** open area, and it is communicated with a negative electrical sink by a copper conductor. The membrane is manufactured by E. I. DuPont de Nemours & Company, Inc. and is sold by them as their XR-type membrane. It is 7 mils thick (about 0.2 mm.) and is joined to a backing or supporting network of polytetrafluoroethylene (Teflon) filaments of a diameter of about 0.1 mm., woven into a cloth which has an area percentage of openings therein of about 22 percent. The membrane is initially flat and is fused onto the screen or cloth of Teflon by high temperature, high compression pressing, with some of the membrane portions actually flowing around the filaments during a fusion process to lock onto the cloth, without thickening the membrane between the cloth filaments, although it is thinned somewhat where it is pressed against the filaments.

The material of the XR-type permselective membrane is a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether. The copolymer is of tetrafluoroethylene and $FSO_2CF_2CF_2OCF(CF_3)CF_2OCF{=}CF_2$ and has an equivalent weight in the 900 to 1,600 range, about **1,250.** The electrodes are each separated about one-eighth inch from the membrane although in some processes this is increased to as much as one-fourth inch (about 6 mm.), with little change in voltage drop.

In a chlorine cell of a type described, rated for the production of **10** tons of chlorine per day and operating at **90%** anode efficiency, a potential drop of **4** volts, a current density of two amperes per square inch, an anolyte NaCl concentration of about 22 percent (25 percent NaCl solution is fed to the anode compartment), an anolyte pH of about 4.5 and an electrolyte temperature of about 90°C., a caustic efficiency of **80%** is obtained and the chlorine cell, in a continuous operation, produces daily 9 tons of sodium hydroxide, **8** tons of chlorine, (containing about 5.3 percent oxygen) and 0.5 ton of sodium chlorate. The hydroxide is an aqueous solution containing 300 g./l. NaOH and about 0.3 g./l. NaCl. The anolyte contains 250 g./l. of NaCl and 100 g./l. of $NaClO_3$.

The anolyte is agitated within the anode compartment, which agitation may be effected by recirculating it to and from such compartment directly, not illustrated in the drawing, so as to help to combat polarization within the compartment. A proportion of the anolyte is removed and fed to a chlorate cell for conversion of chloride therein to chlorate, and for recovery of chlorate produced in the chlorine cell anolyte.

The chlorate cell is a monopolar single-compartment cell having steel walls which serve as the cathode. The anode is platinum-iridium or titanium mesh, like that described for the chloride cell, with the exception that the titanium is coated with a platinum-iridium mixture, containing about three times as much platinum as iridium. The cathode, of mild steel, is like that of the chloride cell. The cell cover is of a plastic or fiberglass reinforced plastic, such as an after-chlorinated polyvinyl chloride, e.g., Trovidur HT, made by Dynamit Nobel, preferably externally reinforced with a polyester resin, more preferably of the chlorendic ester type, e.g., Hetron polyester, made by Hooker Chemical Corp. The chlorate cell, rated at **100** kiloamperes, operates at **4.2** volts and **4** amperes/sq. in. current density and at a temperature of 90°C. 94% Current efficiency is obtained. It produces 1.7 tons per day of sodium chlorate in an aqueous solution containing 430 g./l. of sodium chlorate and 120 g./l. sodium chloride. Bipolar chlorate cells are also used and graphite anodes can be employed. For the metal anodes preferred operating conditions used are pH: 6–6.5; temperature: 60°–80°C.; preferably about **70**°C.; current density: 1–6 a.s.i.; and voltage: 3–4.8 v. For graphite anodes the ranges are 6.5–7; 30°–50°C., preferably about 40°C; 0.5–1.5 a.s.i.; and 3.5–4.5 v.

The aqueous solution of chloride and chlorate removed from the chlorate cell is passed to a separator wherein chloride is removed, and thence to a crystallizer, from which chlorate is removed from the mother liquor. The solid chloride is returned to the anode compartment of the chlorine cell after being passed through the resaturator and is used to increase the chloride concentration of the feed to the anode compartment to about 25 percent sodium chloride. The mother liquor remaining after production of solid sodium chlorate is recycled back to the chlorate cell and includes about one-third of the feed of chloride to the cell. Some of the chlorine produced is burned in hydrogen to make hydrochloric acid, which is utilized to adjust the pH of the anolyte to that desired.

By the described process chloride-free, high strength caustic solution (containing less than 1 percent NaCl, on a solids basis) is made electrolytically in the chlorine cell (because the cationactive permselective membrane prevents chloride ion from entering the catholyte) and the chlorate made in the anode compartment due to reaction of migrating hydroxide is not wasted, being additive to the product of the electrolysis of the chlorine cell anolyte fed to the chlorate cell. The products made, chlorine, caustic and chlorate, are subsequently utilized in the bleaching of groundwood pulps and in processing and pulping operations for the manufacture of papers and paperboard products.

In variations of this process, when the sodium chloride concentration in the chlorine cell anode compartment is varied over the range of from 200 to 320 grams per liter, e.g., 220 g./l. and 310 g./l., the anolyte pH of the chlorine cell is varied over the range of 3 to 7.5, e.g., 4, 5.5 and 7, the temperatures of both cells are varied over the range of 50° to 95°C., e.g., 60°C., **70**°C. and **85**°C., the voltage drops of both cells are varied over the 2.3 to 6 volt range, e.g., 3 and 5 volts for each cell, and the current density is varied in the 0.5 to 6 amperes per square inch range, e.g., 1 and 3 a.s.i. for the chlorine cell and 2 and 6 a.s.i. for the chlorate cell, caustic, chlorine, hydrogen and chlorate are produced at satisfactory rates, with the chlorine containing less than 7.5% of oxygen, the chlorine cell operating at an anode efficiency over 85 percent and a caustic efficiency over 75 percent, and the chlorate cell operating at a current efficiency over 90 percent. Such operating conditions also result when the anode is replaced with a noble metal, a noble metal alloy, a noble metal oxide or a mixture of noble metal oxide and valve metal oxide, e.g., platinum, platinum-ruthenium oxide, platinum-titanium oxides, any of which is a coating on a valve metal such as titanium or tantalum. The cathode is changed to be entirely graphite, iron or steel or to have surfaces of platinum, iridium, ruthenium, rhodium or other noble metal on a base metal, such as copper or steel. Such changes in the electrodes do not adversely affect the operations of the chlorine and chlorate cells or of the overall process of Example 1. Similarly, when the materials of construction of the cell walls are changed to polyvinylidene chloride, synthetic rubber, polypropylene or similar useful substance or other such lining which is resistant to the electrolyte and the electrochemical reaction, the processes are also successful.

EXAMPLE 2

When the cation-active permselective membrane of the chlorine cell of Example 1 is replaced with any of various modifications thereof, having equivalent weights in the 900 to 1,600 range, e.g., 1,100, 1,400, or when the surfaces are modified to a depth of 0.002 or 0.005 mm., as by chemical reactions with pendant groups or additional copolymerizations, utilizing products available from the manufacturer, satisfactory chloride-free caustic having a content of less than 1 percent sodium chloride on a sodium hydroxide solids basis is made and with the modified NF membrane the current efficiency is improved by about 5 percent. Successful processes are also carried out, following the method of Example **1**, when the backing network for the membrane is titanium mesh or polypropylene, FEP or nylon cloth of free area in the range of from 15 to 60 percent, e.g., 15 percent, 30 percent and 55 percent, with filament sizes being about 0.1 mm. Similarly, when the thickness of the membrane is varied to 4 mils or 14 mils, the processes also are operative in the same manner as in Example **1.** Using the thinnest of the mentioned membranes, the backing network may be coated on both sides with the membrane, in a variation of this invention.

EXAMPLE 3

The process of Example **1** is repeated except for the replacement of the membrane with **10** mil membranes identified as 18ST12S and 16ST13S, respectively, made by RAI Research Corporation. The same efficiencies are obtained and satisfactory caustic, chlorate and chlorine production result, as reported in Example **1.** The former of the RAI products is a sulfostyrenated FEP in which the FEP is **18%** styrenated and has two-

thirds of the phenyl groups thereof monosulfonated, and the latter is 16 percent styrenated and has thirteen-sixteenths of the phenyl groups monosulfonated. The membranes do not stand up as well under the described operating conditions as do those of Examples 1 and 2 although they are significantly better for a longer time in appearance and operating characteristics, e.g., physical appearance, uniformity, voltage drop, than the various other cation-active permselective membrane materials available. The membranes do not split in use but do give increased voltage drops as use continues.

The process of this example is carried out as a continuous process, like those of Example 1 and 2 but it is also operative as a batch or once-through process. In such latter methods, as with continuous operations, circulation in the various compartments may be obtained by recirculating the electrolyte (merely removing it from the particular compartment and pumping it back into the compartment).

The invention has been described with respect to working examples and illustrative embodiments but is not to be limited to these because it is evident that one of ordinary skill in the art will be able to utilize substitutes and equivalents without departing from the spirit of the invention or the scope of the claims.

What is claimed is:

1. A method for electrolytically producing chlorate solution, chlorine, hydrogen, and hydroxide solution which comprises electrolyzing 200 to 360 g./l. of aqueous chloride solution having a pH of about 2 to 7 in an electrolytic chlorine cell, said cell having an anode compartment and a cathode compartment, an anode, a cathode, a cation-active permselective membrane of a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether, or of a sulfostyrenated perfluorinated ethylene-propylene polymer, defining a boundary between the anode and the cathode compartments and between the anode and cathode, to produce high-purity hydroxide solution and hydrogen in the cathode compartment and to simultaneously produce chlorate solution and chlorine in the anode compartment, removing high-purity hydroxide solution and anolyte liquor containing chlorate and chloride from the chlorine cell and further electrolyzing the anolyte liquor in a chlorate cell to convert chloride therein to chlorate, while maintaining the temperatures of electrolysis in both cells at less than 105°C.

2. A method according to claim 1 wherein the chlorine cell is of two compartments, the cation-active permselective membrane is of a hydrolyzed copolymer of tetrafluoroethylene and a fluorosulfonated perfluorovinyl ether of the formula $FSO_2CF_2CF_2OCF(CF_3)CF_2OCF{=}CF_2$, which copolymer has an equivalent weight of about 900 to 1,600, the concentration of sodium chloride in the chlorine cell anode compartment is from about 200 to 320 grams per liter, the anolyte pH therein is about 3 to 7, the aqueous hydroxide solution made in the catholyte therein is at a concentration of 250 to 450 g./l., the chlorine made contains less than 7.5 percent of oxygen, the anode efficiency is in excess of 85 percent and the caustic efficiency is greater than 75 percent.

3. A method according to claim 2 wherein the temperatures of electrolysis in both cells are maintained from 50 to 95°C., the voltages are from about 2.3 to 6 volts, the current densities are from about 0.5 to 4 amperes per square inch of electrode surface, the surfaces of the cathodes are of a material selected from the group consisting of platinum, iridium, ruthenium, rhodium, graphite, iron and steel and the surfaces of the anodes are of a material selected from the group consisting of noble metals, noble metal alloys, noble metal oxides, mixtures of noble metal oxides and valve metal oxides, or mixtures thereof, on a valve metal.

4. A method according to claim 3 wherein the permselective membrane is from about 0.02 to 0.5 mm. in thickness and is mounted on a network of material selected from the group consisting of polytetrafluoroethylene, asbestos, perfluorinated ethylene propylene polymer, polypropylene, titanium, tantalum, niobium and noble metals, having an area percentage of openings therein from about 8 to 80%.

5. A method according to claim 4 wherein the copolymer equivalent weight is from about 1,100 to 1,400, the cathode is of steel and the anode is of ruthenium oxide on titanium, the aqueous sodium chloride solution electrolyte in the anode compartment is at a concentration of about 250 to 300 g./l., the pH of the anolyte is about 4.5, the temperatures of the electrolytes are in the range of 65° to 95°C., the membrane wall is from 0.1 to 0.3 mm. thick and the network is a screen or cloth of polytetrafluoroethylene filaments having a thickness of 0.01 to 0.3 mm. and having an area percentage of openings therein of 10 to 70 percent.

6. A method according claim 5 wherein after production of chlorate in the chlorate cell, a solution thereof is withdrawn from the cell, chloride is removed from it and chlorate is crystallized out and the chloride and mother liquor are returned to the anode compartment of the chlorine cell for electrolysis.

* * * * *