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Eng et al.

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[54] **ELECTROLYTIC METHOD FOR THE MANUFACTURE OF HYPOCHLORITES**

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[52] U.S. Cl. **204/95**; 204/257; 204/265

[51] Int. Cl.[2] C25B 1/26; C01B 11/06; C25B 13/08; B01K 1/00

[58] Field of Search 204/86, 87, 92, 93, 295, 204/296

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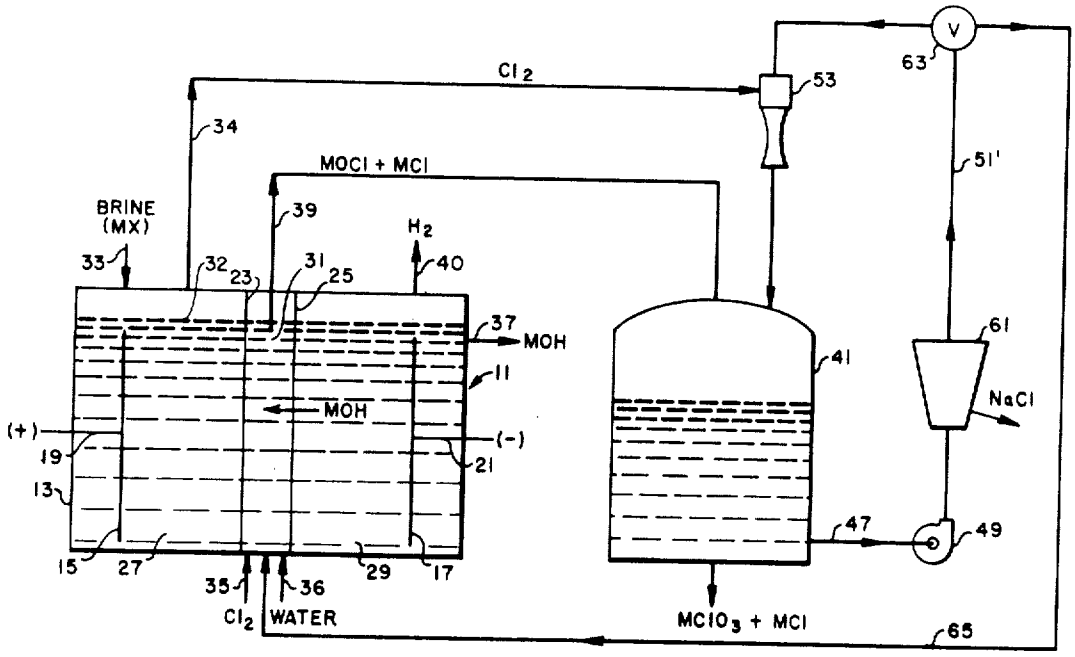
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Primary Examiner—F. C. Edmundson
Attorney, Agent, or Firm—Peter F. Casella

[57] **ABSTRACT**

Hypochlorites, such as alkali metal hypochlorites, are made by electrolyzing brine in a cell having three or more compartments or zones therein, wherein anode and cathode compartments are separated from at least one intervening buffer compartment by cation-active permselective membranes of a hydrolyzed copolymer of tetrafluoroethylene and a fluorosulfonated perfluorovinyl ether or of a sulfostyrenated fluorinated ethylene propylene polymer or by such a permselective membrane on the cathode side plus a porous asbestos diaphragm, while feeding chlorine gas to the buffer zone at such a rate and under such conditions as to produce hypochlorite therein. The hypochlorite may be converted to chlorate externally of the cell or, in a variation of the process, may be converted to chlorate in the buffer compartment.

8 Claims, 3 Drawing Figures



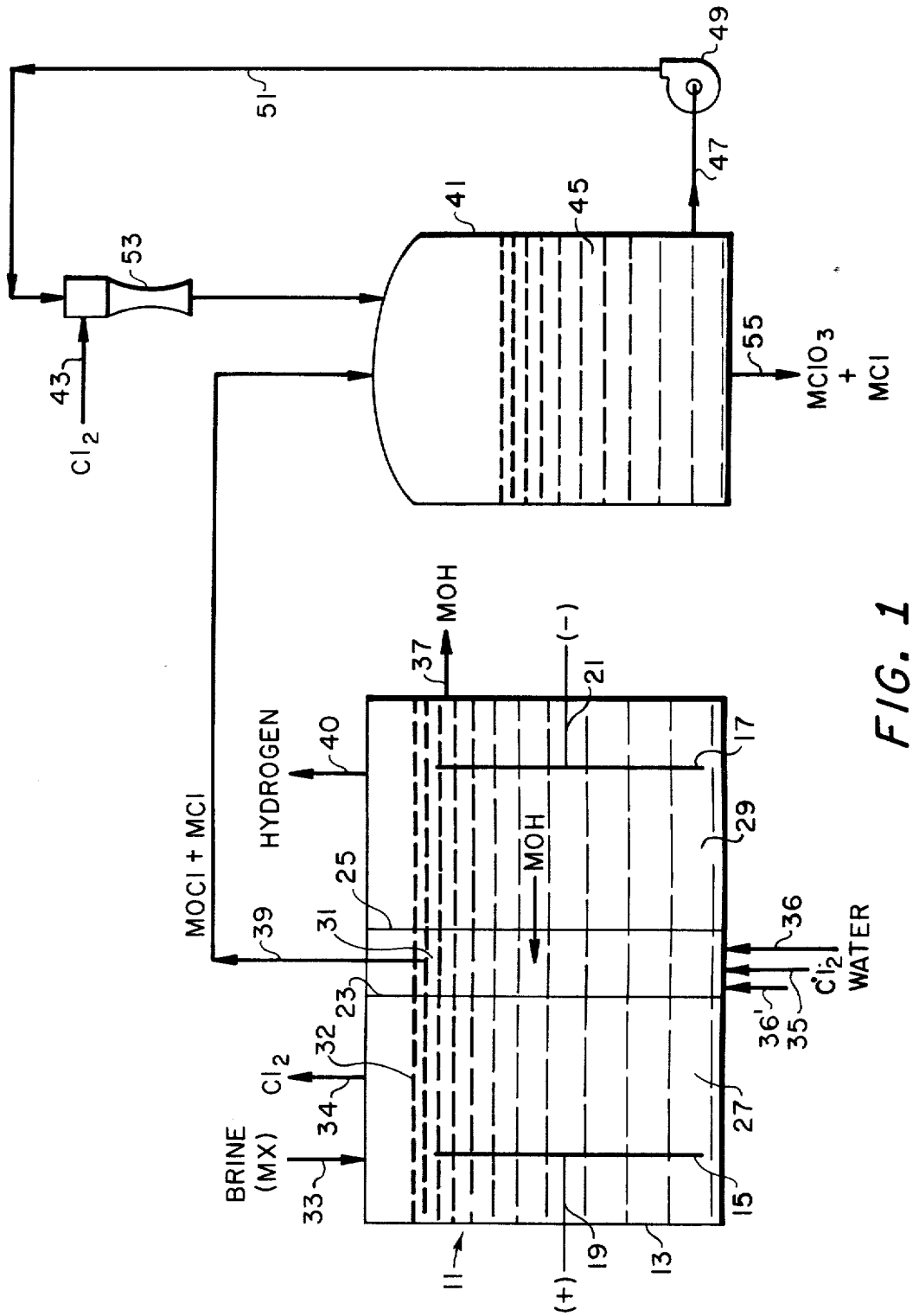

49
51
47
41
45
53
43
Cl_2
55
$MClO_3$ + MCl
MOH
37
(-)
21
HYDROGEN
40
17
MOCl + MCl
39
25
31
MOH
29
36
WATER
Cl_2
36'
35
23
32
Cl_2
34
BRINE (MX)
33
27
15
11
19
(+)
13

FIG. 1

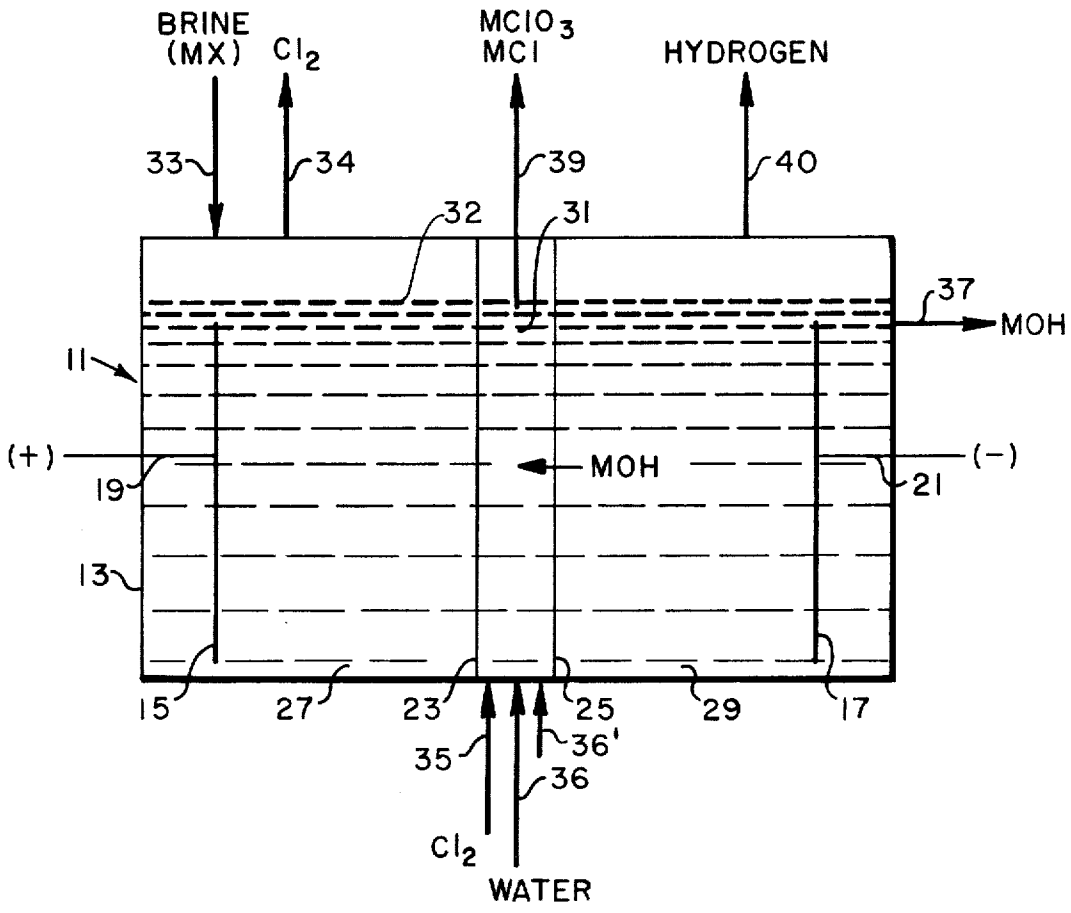

BRINE
(MX)
Cl_2
$MClO_3$
MCl
HYDROGEN
33
34
39
40
32
31
37
MOH
11
(+)
19
MOH
(-)
21
13
15
27
23
25
29
17
35
36'
36
Cl_2
WATER

FIG. 2

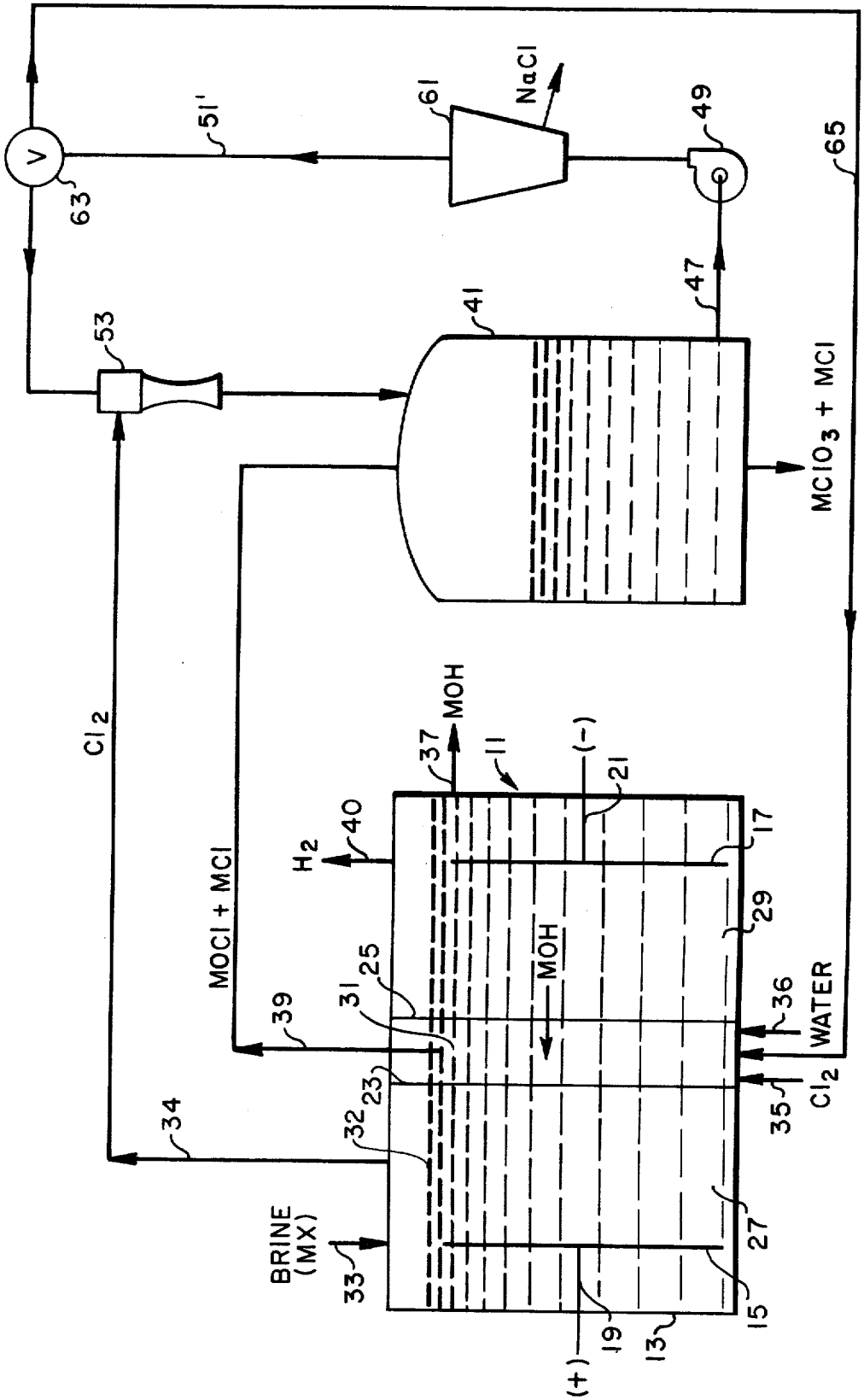

NaCl
61
49
51'
63
65
53
41
47
$MClO_3$ + MCl
Cl_2
MOH
37
11
(-)
21
H_2
40
17
MOCl + MCl
29
MOH
25
31
39
36
WATER
23
Cl_2
35
34
32
BRINE (MX)
33
27
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15
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(+)

FIG. 3

ELECTROLYTIC METHOD FOR THE MANUFACTURE OF HYPOCHLORITES

This invention relates to the electrolytic manufacture of hypochlorites. More specifically, it is of a process for making alkali metal hypochlorite from chlorine and aqueous alkali metal hydroxide solution, both of which reactants are produced in an electrolytic cell containing anode, cathode and buffer compartments, with means provided for separating the cathode and buffer compartments being a cation-active permselective membrane which is a hydrolyzed polymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether or a sulfostyrenated perfluorinated ethylene propylene polymer.

Such cation-permeable membranes permit flow of hydroxyl ion from the catholyte to the buffer zone but do not allow chloride ion to pass through and to mix with the hydroxyl in the cathode compartment. Thus, when chlorine is added to a buffer compartment, hypochlorite is produced therein, consuming the hydroxyl ion and preventing it from flowing to the anolyte and at the same time a chloride-free alkali metal hydroxide is made in the cathode compartment.

Chlorine and caustic, essential and very large volume chemicals required by all industrial societies, are commercially produced by the electrolysis of aqueous salt solutions. Improved electrolytic methods utilize dimensionally stable anodes, which include noble metals, alloys or oxides or mixtures thereof on valve metals. The concept of employing permselective diaphragms to separate anolyte from catholyte during electrolysis is not a new one and plural compartment electrolytic cells have been suggested in which one or more of such membranes is employed. Recently, improved membranes which are of a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether have been described and in some experiments these have been used as the membranes between the catholyte and buffer zones of chlorine-caustic cells. Such membranes have been further improved by surface treatments, preferably by modifications of the sulfonic group, to make them more conductive and efficient. Also, sulfostyrenated perfluorinated ethylene propylene polymers have been made into useful membranes.

Although the electrolysis of aqueous salt solutions is a technologically advanced field of great commercial interest in which much research is performed, and the importance of improving manufacturing methods therein is well recognized, before the present invention the process thereof had not been practiced and the advantages of it had not been obtained.

In accordance with the present invention a method of electrolytically manufacturing a hypochlorite comprises electrolyzing an aqueous solution containing chloride ions in an electrolytic cell having at least three compartments therein, an anode, a cathode, at least one cation-active permselective membrane selected from the group consisting of a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether, and of a sulfostyrenated perfluorinated ethylene propylene polymer, defining a cathode-side wall of a buffer compartment between the anode and cathode, an anode-side wall of said buffer compartment being defined by such a cationactive perselective membrane or a porous diaphragm, and such walls, with

walls thereabout, defining anode, buffer and cathode compartments, while feeding gaseous chlorine into the buffer compartment and regulating the rate of feed thereof and reaction conditions to produce hypochlorite in the buffer compartment. In a preferred embodiment of the invention the permselective membranes are 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 has an equivalent weight of about 900 to 1,600, at least two such membranes are employed, at least one of which separates the anolyte and buffer compartments and the other of which separates the catholyte and buffer compartments, and the membranes are mounted on networks of supporting materials such as polytetrafluoroethylene or asbestos filaments. In some preferred aspects of the invention the hypochlorite is converted to chlorate, either externally or internally of the cell. The described preferred copolymers may be further modified to improve their activities, as by surface treating. modifying the sulfonic group or by other such mechanism. Such varieties of the polymers are included within the generic description given.

The invention will be more readily understood by reference to the following descriptions of embodiments thereof, taken in conjunction with the drawing of apparatuses and means for effecting the invented processes

In the drawing:

FIG. 1 is a schematic representation of the arrangement of equipment for producing hypochlorite is ar electrolytic cell by a method of this invention and subsequently converting it to chlorate outside the cell;

FIG. 2 is a schematic view of an electrolytic cell ir which chlorate is produced internally; and

FIG. 3 is a schematic view of apparatus like that o FIG. 1, including means to remove chloride from the chlorate made and to recirculate chlorate through the cell buffer compartment to increase chlorate content ir the product stream.

In the FIGURES, to facilitate understanding of the process, the flows of typical and preferred reactants and products are illustrated. M stands for alkali metal preferably sodium, but other halide-forming cation may also be employed and in some instances bromine may be at least partially substituted for chlorine.

In FIG. 1 electrolytic cell 11 includes outer wall 13 anode 15, cathode 17 and conductive means 19 and 2 for connecting the anode and the cathode to sources o positive and negative electrical potentials, respectively Inside the walled cell cation-active permselective mem branes 23 and 25 divide the volume into anode or ano lyte compartment 27, cathode or catholyte compart ment 29 and buffer compartment 31. An acidic aque ous solution 32 of alkali metal halide is fed to the ano lyte compartment through line 33 and chlorine gas i fed to the buffer compartment through line 35. Recir culated buffer solution may also be fed into the buffe compartment, through a separate line, 36' or a com mon line with the chlorine or water. Water may be ad mitted through line 36 to maintain the desired liqui level in the buffer compartment. Of course, liquid lev els should be maintained in all compartments and this i often effected with known feed-overflow technique the apparatus for effecting which is known and there fore, is not illustrated.

Halogen, e.g., chlorine gas, is removable from the ar olyte compartment through line 34 and aqueous so dium hydroxide is removable from the catholyte com

partment through line **37**. An aqueous solution of alkali metal hypochlorite, with some dissolved alkali metal chloride, is removable through line **39** and may be passed through that line to reaction vessel or mixer **41** in which it is mixed with halogen, e.g., chlorine gas, from line **34**. The chlorine passes through line **43**, and may be pulled through that line by low pressure created by pumping hypochlorite-chloride or hypochlorite-chlorate-chloride solution **45** through line **47**, pump **49** and return line **51**, through eductor reactor **53**, in which intimate mixing is effected. Chlorine gas in the upper portion of reaction and retention vessel **41** may be vented off or may be recycled, too, The chlorate made is removed as an aqueous solution, with alkali metal chloride, through discharge line **55**. The chlorate-chloride solution may be circulated through lines **47** and **51**, pump **49**, reactor **53** and vessel **41** until the chlorate-chloride concentration is increased to a useful level. Chloride may be removed by precipitation and if desired, chlorate may be crystallized out by installation of the appropriate apparatus in lines **47** and **51**. Because sodium chloride is relatively insoluble, compared to sodium chlorate, it should be removed before chlorate crystals are manufactured; otherwise chloride solids can block orifices, etc., during manufacturing.

In some aspects of the invention, when it is preferred to produce the hypochlorite for direct use, it is removed through line **39**, together with alkali metal chloride. Some of it may subsequently be converted to chlorate. Hydrogen is obtainable from line **40**.

In the operation of the invented process chlorine is generated at the anode and alkali metal hydroxide and hydrogen are produced at the cathode. The normal tendency for alkali metal halide to move into the catholyte and increase the halide content of the hydroxide made is counteracted by the cationic permselective membrane **25** and this prevention of chloride flow is aided by the presence of the additional permselective membrane **23**. Yet, alkali metal hydroxide may migrate from catholyte to the anolyte in ordinary cells and such migration can interfere with the caustic or sodium ion current efficiency if the product made is useless or is not recovered. Caustic, sodium ion or cathode current efficiency is the percentage of useful product made, compared to 100% maximum, with the current flow employed. Sodium ion efficiency may be the most exact of the terms employed but all are used. Thus, if sodium hydroxide is chemically reacted to make recoverable sodium hypochlorite or sodium chlorate, coulombs are not wasted, as they are when hydroxyl ions are electrolytically converted to useless oxygen at the anode. Anode or chlorine efficiencies are figured in the same general way.

In the present cell the addition of chlorine to the buffer zone causes the alkali metal hydroxide migrating through the membrane, as illustrated, to be converted to hypochlorite and chloride, which do not pass through the permselective membranes. Therefore, the process satisfactorily produces a chloride-free caustic at satisfactory high current efficiency and additionally makes a desired byproduct, the hypochlorite, which may be further converted to chlorate, when desired.

In FIG. **2** the manufacture of chlorate in the buffer zone is shown, using a cell like that of FIG. **1**. The only difference in operation is in the employment of sufficient chlorine to diminish the pH further, favoring formation of chlorate rather than of hypochlorite, which is normally produced at a higher pH. Acids and bases may also be used to regulate the pH. A liquid medium such as recirculated buffer solution or other chlorate-chloride-water solution may be added to the buffer zone through line **36** so as to help control the temperature, and sometimes, to increase the percentage of chlorate in the buffer zone and in the recirculating liquid to such a level that after removal of chloride, chlorate may be crystallized out.

In FIG. **3** external manufacture of chlorate is illustrated, with buildup of chloride and chlorate concentrations by recirculation, followed by removal of the chloride, which may then be followed by crystallization of the chlorate. As is illustrated, chloride-chlorate solution may be recirculated through vessel **41** via lines **47** and **51'** with the solution passing through pump **49** and reactor **53**. During recirculation additional reaction with MOCl from the cell is effected in reactor **53** and the concentrations of the hypochlorite and chloride resulting from such reaction are increased. Because the chloride is less soluble and is produced to a greater extent, it will soon crystallize out in the reactor or retention vessel, causing processing difficulties. Accordingly, it is removed in separator or crystallizer **61** and more pure, more concentrated chlorate is continually circulated and ultimately, is drawn off from the retention vessel **41**, possibly for further concentration and/or crystallization out as the solid. At junction **63** a proportioning valve may be located and the concentration of chlorate in the circulating system may be further increased by returning a proportion of it through line **65** to cell **11**. Desired pH's at various parts of the system may be controlled by regulating the proportions of chlorine utilized at such different locations.

Although some circulations and recirculations of materials of the process are illustrated, others may also be effected. Thus, anolyte, buffer compartment solution and catholyte recirculation may be utilized to maintain the various solutions at the same concentrations throughout their respective compartments. Alternatively, once-through processes and "hybrid" processes are also useful. Similarly, recirculation of chlorate-chloride solutions may be to the anolyte compartment, at least in part, to convert the chloride thereof to chlorine and thus reduce the concentration of it in the chlorate-chloride mixtures.

In the preferred embodiments of the invention the buffer zone or compartment has two opposing boundaries or walls thereof, dividing it from anode and cathode compartments, respectively, both of the described hydrolyzed copolymer membranes, usually supported on an open network, screen or cloth of electrolyte- and product-resistant material which is preferably filamentary in form. The cationic membranes oppose or prevent the passage of anions such as halide, hypohalite and halate ions, while allowing the passage of cations, e.g., alkali metal and hydrogen ions. Low molecular weight anions, such as hydroxyl, may also pass through the cationic membranes.

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 their unexpectedly beneficial effects 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 and replacement of the membrane, while all the time it efficiently prevents

undesirable migration of hypochlorite from the buffer compartment and prevents the chloride ions of the anolyte from entering the buffer compartments, while also stopping any chloride in the buffer zone from transferring to the catholyte. Together with the use of the buffer zone between the anolyte and catholyte zones, it prevents hydrogen formed on the cathode side from escaping into the halogen formed on the anode side. In this respect the present membranes are superior to prior art membranes because they are more impervious to the passage of hydrogen, even in comparatively thin films, than are various other polymeric materials. Also important is their ability to prevent transfer of chlorine gas into the hydrogen produced at the cathode, especially when chlorine is fed to the buffer compartment, since when chlorine is present in hydrogen an explosive mixture may be formed. The superiority of the preferred membranes of the described copolymer (including modified or surface treated versions thereof) over the prior art membranes in the various described aspects is also evident, usually to a lesser degree, in the sulfostyrenated fluorinated ethylene propylene polymers.

Although the preferred embodiments of the invention utilize a pair of the described membranes to form the three compartments of the present cells it will be evident that a greater number of compartments, e.g., 4 to 6, including plural buffer zones, may be employed. Similarly, also, while the compartments will usually be separated by flat membranes and will usually be of substantially rectilinear or parallelepipedal construction, various other shapes, including curves, e.g., ellipsoids, irregular surfaces, e.g., sawtoothed or plurally pointed walls, may also be utilized. In another variation of the invention the buffer zone(s), formed by the plurality of membranes, will be between bipolar electrodes, rather than the monopolar electrodes which are described herein. Those of skill in the art will know the variations in structure that will be made to accommodate bipolar, rather than monopolar electrodes, and therefore, these will not be described in detail. Of course, as is known in the art, pluralities of the individual cells will be employed in multi-cell units, often having common feed and product manifolds and being housed in unitary structures. Again, such constructions are known to those in the art and need not be discussed herein.

For most satisfactory and efficient operations the volume of the buffer compartment(s) will usually be from 1 to 100%, preferably from 10 to 70% that of the sum of the volumes of the anode and cathode compartments.

Although the utilization of the present cationic or cation-active membranes to define the buffer compartment(s) and separate it/them from the anolyte and catholyte sections is highly preferred it is possible to operate with a conventional diaphragm separating the anode compartment from the buffer compartment. However, the membrane will be employed to separate the catholyte from the buffer zones in order to produce the highly desirable salt-free caustic. Otherwise, even if such a membrane was employed to separate the anolyte from the buffer zone, halide present in the buffer section due to addition of brine or production by the reaction of chlorine with the caustic to form hypochlorite, could pass through the diaphragm to contaminate the caustic. In many applications salt-free caustic is highly desirable and therefore, 3-compartment cell structures having a cathode-side porous diaphragm, such as illustrated in the U.S. Environmental Protection Agency publication entitled *Hypochlorite Generator for Treatment of Combined Sewer Overflows* (Water Pollution Control Research Series 11023 DAA 03/72) are unsatisfactory. Additionally, the conventional diaphragms which are usually of deposited asbestos fibers, tend to become blocked with insoluble impurities from the brine and have to be cleaned periodically, usually necessitating shutdown of the cell and often, replacement of the diaphragm.

The aqueous solution containing chloride ions is normally a water solution of sodium chloride, although potassium and other soluble chlorides, e.g., magnesium chloride and ammonium chloride, may be utilized, at least in part. However, it is preferable to employ the alkali metal chlorides and of these sodium chloride is the best. Sodium and potassium chlorides include cations which form soluble salts or precipitates and which produce stable hydroxides. The concentration of sodium chloride in a brine charged 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 intermediate figures for mixtures of sodium and potassium chlorides. The electrolyte may be neutral or acidified to a pH in the range of about 2 to 6, acidification normally being effected, with a suitable acid such as hydrochloric acid. Charging of the brine is to the anolyte compartment. The solid sodium chloride added to the liquid medium in the anolyte results in a sodium chloride concentration from 200 to 320 g./l. and most preferably of 250 to 300 g./l. In recycle charges to the buffer compartment, if utilized, the concentration will normally be less than 50 or 100 g./l., although chlorate contents may be higher and usually the chloride contents of the buffer liquids will be less than such limits, too.

Water may be charged to the buffer compartment and in some cases it may be desirable to charge water with brine to the anolyte compartment. Dilute caustic may be recirculated to the catholyte compartment but this is not usually done. For the most part the liquid level in that zone is maintained by transfer to it of material(s) charged to the anolyte and/or buffer zone, plus water.

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_2–$CF_2OCF(CF_3)CF_2OCF{=}CF_2$. 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 perfluoro-lower 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 aqueous 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%, preferably 15 to 20% and most preferably about 17%. 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% 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. No. 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 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 membranes 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 does 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 produced by the present method 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 electro-chemical 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 or may be replaced in part with other moieties. Such changes 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%, often about 5 to 15%. Exemplary of such treatments is that described in French Pat. No. 2,152,194 of Mar. 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 3 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 megarads. After rinsing with water the phenyl rings of the styrene portion of the polymer are monosulfonated, preferably in the para position, 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 ½ 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% styrenated and having ⅝ of the phenyl groups monosulfonated and the latter being 16% styrenated and having 13/16 of the phenyl groups monosulfonated. To obtain 18% styrenation a solution of 17-½% of styrene in methylene chloride is utilized and to obtain the 16% styrenation a solution of 16% 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 walls 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%, preferably 10 to 70% and most preferably 30 to 70%. 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. It is preferred to employ the described backed membranes as walls of the cell between the anolyte and catholyte compartments and the buffer compartment(s) but if desired, that separating the anolyte and buffer compartments may be of conventional diaphragm material, e.g., deposited asbestos fibers or synthetic polymeric fibrous material (polytetrafluoroethylene, polypropylene). Also, treated asbestos fibers may be utilized and such fibers mixed with synthetic organic polymeric fibers may be employed. However, when such diaphragms are used efforts should be made to remove hardness ions and other impurities from the feed to the cell so as to prevent these from prematurely depositing on and blocking the diaphragms.

The material of construction of the cell body may be conventional, including 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 electrodes of the cell can be made of any electrically conductive material which will resist the attack of the various cell contents. In general, the cathodes are made of graphite, iron, lead dioxide on graphite or titanium, steel or noble metal, such as platinum, iridium, ruthenium or rhodium. Of course, when using the noble metals, they may be deposited as surfaces on conductive substrates, e.g., copper, silver, aluminum, steel, iron. The anodes are also of materials or have surfaces of materials such as noble metals, noble metal alloys, noble metal oxides, noble metal oxides mixed with valve metal oxides, e.g., ruthenium oxide plus titanium dioxide, or mixtures thereof, on a substrate which is conductive. Preferably, such surfaces are on or with a valve metal and connect to a conductive metal, such as those previously described. Especially useful are platinum, platinum on titanium, platinum oxide on titanium, mixtures of ruthenium and platinum and their oxides on titanium and similar surfaces on other valve metals, e.g., tantalum. The conductors for such materials may be aluminum, copper, silver, steel or iron, with copper being much preferred. A preferable dimensionally stable anode is ruthenium oxide-titanium dioxide mixture on a titanium substrate, connected to a copper conductor.

The voltage drop from anode to cathode is usually in the range of about 2.3 to 5 volts, although sometimes it is slightly more than 5 volts, e.g., up to 6 volts. Preferably, it is in the range of 3.5 to 4.5 volts. The current density, while it may be from 0.5 to 4 amperes per square inch of electrode surface, is preferably from 1 to 3 amperes/sq. in. and ideally about 2 amperes/sq. in. The voltage ranges given are for perfectly aligned electrodes and it is understood that where such alignment is not exact, as in laboratory units, the voltages can be up to about 0.5 volt higher.

The feeding of gaseous chlorine into the buffer compartment is at such a rate as to enable it to react with the sodium hydroxide entering such compartment from the catholyte and to convert substantially all of it to hypochlorite (or further, to chlorate), thereby preventing it from migrating further into the anolyte. It will be evident that the rate of feed is controlled in response to variations in caustic transmission into the buffer compartment. Additions may be in response to pH fluctuations in the buffer zone. Normally, to produce hypochlorite, possibly with some chlorate therein, in the buffer zone, a pH of 8 to 11 will be maintained whereas to produce chlorate therein this will be lowered to 6 to 7.5, preferably 6 to 7. Control of the pH may be and preferably is by chlorine addition but other acidifying agents may be employed, also. On the average, it is considered that from 5 to 20% of the caustic produced in the catholyte compartment migrates to the buffer compartment and therefore, the stoichiometric amount of chlorine to convert this caustic to hypochlorite will be employed, plus an excess when desired, e.g., from 5 to 20% of chlorine, to adjust the pH. In addition to controlling the pH of the buffer zone electrolyte to obtain the desired product, temperature is also controlled. Normally, it is maintained at less than 105°C., preferably being from 20° to 95°C., more preferably, 50° to 95°C. and most preferably, about 60 to 85°C. or 95°C. Similar temperatures apply to the electrolyte in the anolyte and catholyte compartments. However, the pH of the buffer solution and catholyte are different from those of the anolyte, being about 14, compared to about 1 to 5, preferably 2 to 4 for the anolyte. The temperature of the electrolyte may be controlled by recirculation of various portions thereof, in the anolyte catholyte and buffer zones. Also, it is affected by the proportion of feed to such zones and the temperatures thereof. Feeds will be regulated to obtain the desired temperatures, previously mentioned. Of course, where the temperature cannot be lowered sufficiently by recirculation, refrigeration of the recirculating liquid may also be utilized. For example, the feeds of water, brine and recirculated electrolyte or mixtures of these entering the anode compartment or any of the other compartments may be cooled about 5° to 40°C. below their otherwise obtained temperatures or to about 10°C. before admissions to such compartment(s).

When the hypochlorite is being produced in the buffer compartment or a mixture of hypochlorite and chlorate is being made therein the hypochlorite content may be converted to chlorate externally of the cell by addition of chlorine or other acidifying agent to lower the pH from 8 to 11 to the range of 6 to 7.5, preferably 6 to 7. The chlorine employed is chlorine produced in the cell. It is a preferred acidifying agent for this reason and because byproduct chloride can be reused. Whether the chlorate is made externally or internally or whether the hypochlorite is removed for use, excess chlorine sent to the buffer zone is also recoverable and reusable. Similarly, if chlorate is recovered from the liquid product the aqueous medium may be returned to the buffer zone, preferably after removal of chloride, too.

The processes of this invention realize greatly improved current efficiencies due to their prevention of the wasteful production of oxygen in the anolyte compartment. Anolyte pH is kept low, to prevent oxygen release, by neutralization of hydroxyl ions and in the present process the chlorine in the buffer solution diminishes hydroxyl in the anolyte markedly. Thus, chlorine current efficiencies of from 90 to 97% are obtainable, together with caustic current efficiencies of from 75 to 85% or higher. Also, the caustic made is free of chloride, normally containing as little as 0.1 to 10 g./l. thereof. The hypochlorite concentration will normally be from 50 g./l. to its solubility limit and the chlorate concentration producible, either in the cell or external thereto, is 150 to 450 g./l. The sodium hydroxide concentration from the catholyte can be increased by feeding dilute sodium hydroxide, recirculating sodium hydroxide solution previously taken off, increasing the electrolysis time or diminishing the rate of caustic takeoff. Alternatively, more concentrated caustic solutions may be made by evaporation of comparatively dilute solutions produced. When more concentrated caustic is made in the catholyte the hpochlorite or chlorate made in the buffer zone will also be more concentrated.

The present cells may be incorporated in large and small plants, those producing hypochlorite or chlorate while also making from 20 to 1,000 tons per day of chlorine or equivalent and in all cases efficiencies obtainable are such as to make the process economically desirable. It is highly preferred however, that the installation should be located near to and be used in conjunction with a pulp bleaching plant, so that the hypochlorite or chlorate can be employed as a bleach or in the production of bleaching agent, e.g., chlorine dioxide.

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

To produce hypochlorite electrolytically and externally convert it to chlorate the apparatus illustrated in FIG. 1 is employed, with the electrolytic cell having steel walls. The anode compartment is lined with polyester resin and the buffer compartment is lined with polypropylene. The anode is of an expanded diamond-shaped titanium mesh (1 mm. in thickness and expanded to 50% open area with strand thickness and width being equal), coated with a mixture of ruthenium oxide and titanium oxide 0.1 mm. thick, in a ratio of 1:3. The titanium mesh is communicated with a positive direct current electrical source through a titanium-clad copper conductor. The cathode is of mild steel woven wire mesh 2.2 mm. in diameter and 6 × 6 to the inch and is communicated to a negative electrical source or sink by a copper conductor. The walls separating the anode and cathode compartments, and together with walls of the cell, defining the buffer compartment, are of a cation-active permselective membrane manufactured by E. I. DuPont de Nemours & Company and sold under the trade name Nafion. Characteristics of such membranes are described in a DuPont New Product Information Bulletin of 10/1/69 under the title *XR Perfluorosulfonic Acid Membranes.* The walls of the membrane are seven mils thick (about 0.2 mm.) and it is joined to a backing or supporting network of polytetrafluoroethylene (Teflon) filaments having a diameter of about 0.1 mm. and arranged in a screen or cloth form so that the area percentage of openings therein is about 25%. The cross-sectional shape of the filaments is substantially circular and the membranes mounted on them are originally flat and are fused onto the screen or cloth by high temperature, high compression pressing, with some of the membrane actually flowing around the filaments during the fusion process to lock onto the cloth.

The material of the premselective membrane is a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether. The hydrolyzed 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.

In the electrolytic cell illustrated in FIG. 1, for clarity of presentation and in accord with conventional cell illustrations, spaces are shown between the buffer compartment membranes and the electrodes but in the practice of this experiment the electrodes are in contact with the buffer membranes, with the "flatter" sides of the membranes facing the contacting electrodes. The buffer compartment between them is ¼ inch (6.4 mm.) wide, for minimum voltage drop at satisfactory production rates and the interelectrode distance is essentially the same, although gaps of 7/16 inch are also successfully used.

The anode compartment is filled with a saturated salt solution or brine and the cathode and buffer compartments are filled with water, initially containing a small quantity of salt or brine to improve conductivity. Then the current is turned on and chlorine is fed to the buffer compartment to convert any sodium hydroxide transmitted thereto to sodium hypochlorite and sodium chloride. Chlorine is removed from the anode compartment and, in addition to being taken off for use or sale as chlorine, some thereof is fed to the buffer compartment and an additional proportion is utilized to help to convert sodium hypochlorite to sodium chlorate externally of the cell. Hydrogen gas is removed from the cathode compartment and, after it reaches a satisfactory concentration, sodium hydroxide is also taken off from that compartment and is essentially free of chloride ions, containing about 1 g./l. of sodium chloride.

During operation of the cell the pH in the buffer compartment is maintained in the range of 8 to 11, at about 10, to promote formation of hypochlorite. Control of the pH in the buffer compartment is maintained by adjusting the feed of chlorine and to some extent, water. The pH in the anode compartment is held at about 4 and acidification control is maintained by addition of small proportions of hydrochloric acid. Of

course, the pH in the cathode compartment is 14.

The solution of sodium hypochlorite and sodium chloride is conveyed from the electrolytic cell to a retention vessel from which it is pumped continuously in a cycle through a reactor wherein the hypochlorite is treated with chlorine to produce sodium chlorate and more sodium chloride. The mixture is drawn off from the retention vessel and the sodium chloride is subsequently separated from the sodium chlorate so that the chlorate may be utilized in pulp bleaching without stream pollution by the accompanying chloride.

In a modification of the described process means are provided for removing sodium chloride from the circulating stream from the retention vessel and chlorate liquor, essentially free of chloride is partly returned to the retention vessel through the reactor, where a small proportion of sodium hypochlorite present therein is reacted with chlorine to produce additional chlorate, and another portion of the chloride-free chlorate is removed from the system, to be crystallized to solid chlorate or to be employed as a chlorate liquor. When crystallized, the mother liquor is returned to the buffer compartment of the electrolytic cell. The following table describes the operation of the process (unmodified) of this example in a number of variations of the described process.

TABLE 1

	EXAMPLES				
	1-1	1-2	1-3	1-4	1-5
Average Anolyte NaCl Conc. (g./l.)	270.0	270.0	270.0	270.0	270.0
Av. Anolyte $NaClO_3$ Conc. (g./l.)	< 1 g./l.	< 1 g./l.	< 1 g./l.	< 1 g./l.	< 1 g./l.
Av. Buffer Compartment NaOH Conc. (g./l.)	36.20	21.80	48.32	58.12	19.32
Av. Catholyte NaOH Conc. (g./l.)	339.80	238.40	325.68	395.36	236.88
Av. Catholyte $NaClO_3$ Conc. (g./l.)	1.3	2.95	0.80	0.45	2.65
Av. Catholyte NaCl Conc. (g./l.)	0.78	1.33	1.27	1.40	2.76
Av. Anolyte Flow Rate (l./min.)	0.81	0.76	0.94	0.80	0.95
Av. Buffer Inlet Flow Rate (ml./min.)	20.0	19.5	19.8	—	—
Av. Buffer Exit Flow Rate (ml./min.)	19.1	19.5	19.0	20.0	15.2
Av. Catholyte Exit Flow Rate (l./min.)	0.151	0.115	0.082	0.054	0.438
Anolyte Volume in System (l.)	121.910	118.339	123.695	121.650	24.000
Anode Compartment Volume (l.)	3.840	3.840	3.840	3.840	3.840
Cathode Compartment Volume (l.)	3.884	3.884	3.884	3.884	3.884
Buffer Compartment Volume (l.)	0.520	0.520	0.520	0.520	0.520
Av. Anolyte Temperature (°C.)	72	72	64	81	95
Av. Anolyte pH	4.47	3.90	4.40	5.35	3.95
Av. Catholyte Temperature (°C.)	68	63	54	79	81
Av. Current Density (a.s.i.)	1.204	1.052	0.740	1.500	1.667
Av. Cell Voltage	5.163	4.943	4.798	5.407	4.894
Anode NaCl Efficiency (%)	97.70	92.26	91.81	92.34	87.2.
Anode Current Efficiency (%, from gas analysis)	94.10	92.82	—	—	90.69
NaOH Accounted for (or NaOH Efficiency, %)	98.36	92.46	99.56	97.27	91.38
$NaClO_3$ Efficiency (%)	95.40	90.72	98.54	93.67	90.99
Operational Cell Time (hours)	23.00	19.00	22.50	16.08	3.00

EXAMPLE 2

In the procedure described the feed of sodium chloride to the anolyte compartment is at about 25% sodium chloride concentration and in the effluent from the anolyte the chloride concentration is about 22%. The chloride-free caustic is taken off from the cathode compartment and the buffer compartment material is either employed as hypochlorite or, as illustrated in FIG. 1, is fed to a reactor and then to a holding tank equipped with means to lower the chloride concentration during recirculation. In the holding tank, wherein the pH is held at 6.5, the hypochlorite is converted to chlorate with a typical concentration and that of this example being 430 g./l. of sodium chlorate, with 140 g./l. sodium chloride. In some runs as much as 500 g./l. of the chlorate and as little as 100 g./l. of the chloride are produced. The hypochlorite and chlorate produced are used in bleaching of groundwood pulp and greatly improve the color thereof.

In a modification of the preceding process the apparatus of FIG. 2 is employed and the rate of chlorine feed to the buffer compartment is regulated so that the pH of the buffer solution is maintained at about 6.5, at which pH the hypochlorite is converted to chlorate in the buffer compartment. Otherwise, the experiments are essentially the same and the product resulting is the same.

EXAMPLE 3

The procedure of Example 1 is followed with the exception that the apparatus of FIG. 3 is employed and sodium chloride is continuously removed from recirculating chlorate, which circulates through a chloride removal apparatus and also back to the buffer compartment. By this method chlorate is continuously removed from the holding vessel and chloride content is maintained low enough so that it does not crystallize out in the cell or other portions of the apparatus.

EXAMPLE 4

Using a commercial size three-compartment cell like that of FIG. 1 chlorate is formed externally at the rate of 0.42 ton per day of sodium chlorate, at 95% conversion, maintaining the buffer compartment pH at about 10.5 and the reactor and holding vessel pH at about 6.5. The current is 90 kiloamperes and the current density is 2 amperes/sq. in., at a direct current potential of 4.5 volts and at 70°C., and the process is continuous. The chlorine feed to the buffer compartment is at the rate of 0.89 ton perday of the 3 tons per day of chlorine produced at the anode at 95% current efficiency. Sodium hydroxide produced is at a 25% concentration and is made at the rate of 2.28 tons per day. Sodium chloride solution charged to the anode compartment is a 25% solution and the concentration of sodium chloride in the effluent from that compartment is 22%.

EXAMPLE 5

Using a commercial apparatus like that of FIG. 2 and maintaining the buffer compartment pH at 6.5, 0.4 ton per day of sodium chlorate is made in situ in the buffer compartment at a 90% conversion rate. A small pro-

portion (about 5%) of hypochlorite is present in the product. The pH is maintained by addition of more chlorine to the compartment. Other conditions are the same as described in Example 4. In a modification a batch process is employed with essentially the same results. When in place of the described membrane there are substituted 18ST12S and 16ST13S RAI membranes of about twice the thickness of the XR perfluorosulfonic acid membranes employed in the other examples the same reactions are effected and the desired products also result. However, in such cases it is noted that the RAI membranes are not as resistant to the electrolyte and the products of electrolysis and do not last as long in use until replacement becomes desirable. This is especially true when thinner membranes, such as those of 7 mil thickness are employed.

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 manufacturing a hypochlorite which comprises electrolyzing an aqueous solution containing chloride ions in an electrolytic cell having at least three compartments therein, being anode and cathode compartments and at least one buffer compartment, an anode, a cathode, at least one cation-active permselective membrane selected from the group consisting of a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether, and a sulfostyrenated perfluorinated ethylene propylene polymer, defining a cathode-side wall of a buffer compartment between the anode and cathode, an anode-side wall of a buffer compartment being defined by such a cation-active permselective membrane or a porous diaphragm, and such walls, with walls thereabout, defining anode, cathode and buffer compartments, while feeding gaseous chlorine into a buffer compartment and regulating the rate of feed thereof and reaction conditions to produce hypochlorite in the buffer compartment.

2. A method according to claim 1 wherein the permselective membrane(s) is/are of a hydrolyzed copolymer of tetrafluoroethylene and a sulfonated perfluorovinyl ether of the formula $FSO_2CF_2CF_2OCF(CF_3)CF_2OCF{\times}CF_2$, which copolymer has an equivalent weight of about 900 to 1,600.

3. A method according to claim 2 wherein the pH of the aqueous buffer compartment solution is maintained in the range of about 6 to 11, the temperature thereof is less than about 105°C. and the cell contains a single buffer compartment.

4. A method according to claim 3 wherein the anode side and cathode side walls of the buffer zone are of the permselective membrane, which is of a hydrolyzed copolymer of tetrafluoroethylene and a sulfonated perfluorovinyl ether of the formula of claim 4, the membrane walls are from about 0.02 to 0.5 millimeter thick and the buffer solution pH is from 8 to 11.

5. A method according to claim 4 wherein the membranes are mounted on a netework of a material selected from the group consisting of polytetrafluoroethylene, asbestos, perfluorinated ethylene propylene polymer, polypropylene, titanium, tantalum, niobium and noble metals, which has an are percentage of openings therein from about 8 to 80%.

6. A method according to claim 5 wherein the temperature is from 60° to 95°C., the network is a screen or cloth of polytetrafluoroethylene filaments having a thickness of 0.01 to 0.5 mm., being less than or equal to the thickness of the membrane mounted thereon and the area percentage of openings in the screen or cloth is from about 10 to 70%.

7. A method according to claim 6 wherein the membrane walls are from 0.1 to 0.3 mm. in thickness and the temperature of the electrolyte is regulated at least in part by the recirculation of compartment contents.

8. A method according to claim 1 wherein the hypochlorite made is sodium hypochlorite and chloride ions are from sodium chloride.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,925,174

DATED : December 9, 1975

INVENTOR(S) : Jeffrey D. Eng et al.

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

Column 1, line 67, "cationactive perselective" should read ---cation-active permselective---;

Column 6, line 53, "2 to " should read---2 to 3---;

Column 7, line 38, "into spaces" should read---into the spaces---;

Column 12, line 12, "Premselective" should read ---perm-selective---;

Column 14, line 56, "perday" should read--- per day---;

Claim 2, line 7 "$CF_2OCFXCF_2$" should read---$CF_2OCF=CF_2$---;

Signed and Sealed this

Twenty-third Day of November 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks