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[54] **ELECTROLYTIC MANUFACTURE OF DITHIONITES**

[75] Inventors: **Jeffrey D. Eng**, North Vancouver; **Cyril J. Harke**, Burnaby, both of Canada

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

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[58] **Field of Search**..... 204/92, 98, 128

[56] **References Cited**

UNITED STATES PATENTS

3,220,941	11/1965	Osborne	204/92
3,344,053	9/1967	Neipert et al.	204/266
3,523,755	8/1970	Mc Rae	204/92 X
3,784,399	1/1974	Grot	260/79.3 MU

FOREIGN PATENTS OR APPLICATIONS

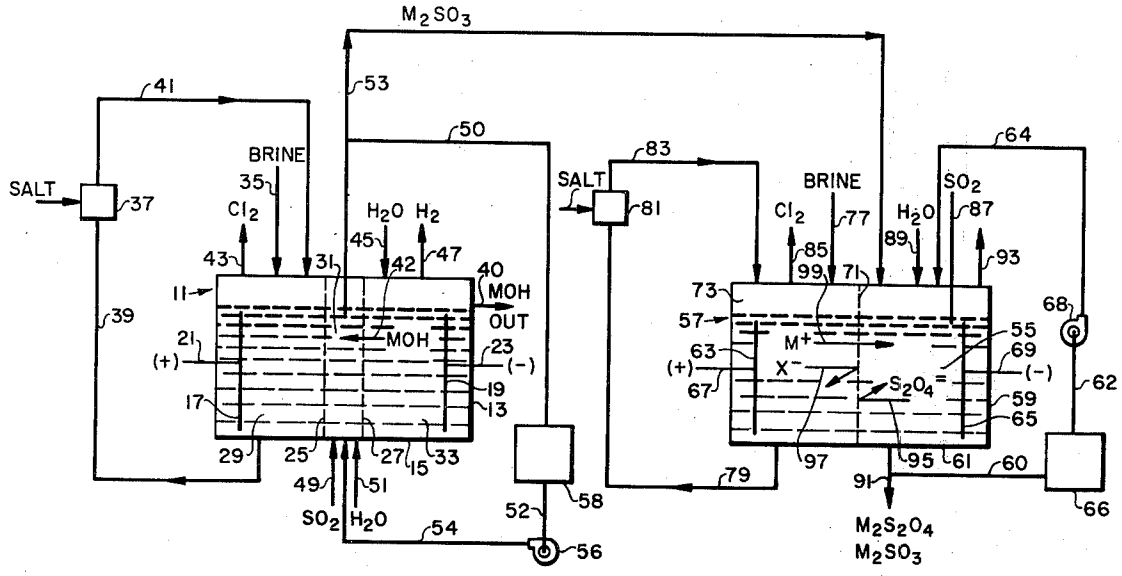
1,045,675	10/1966	United Kingdom	204/92

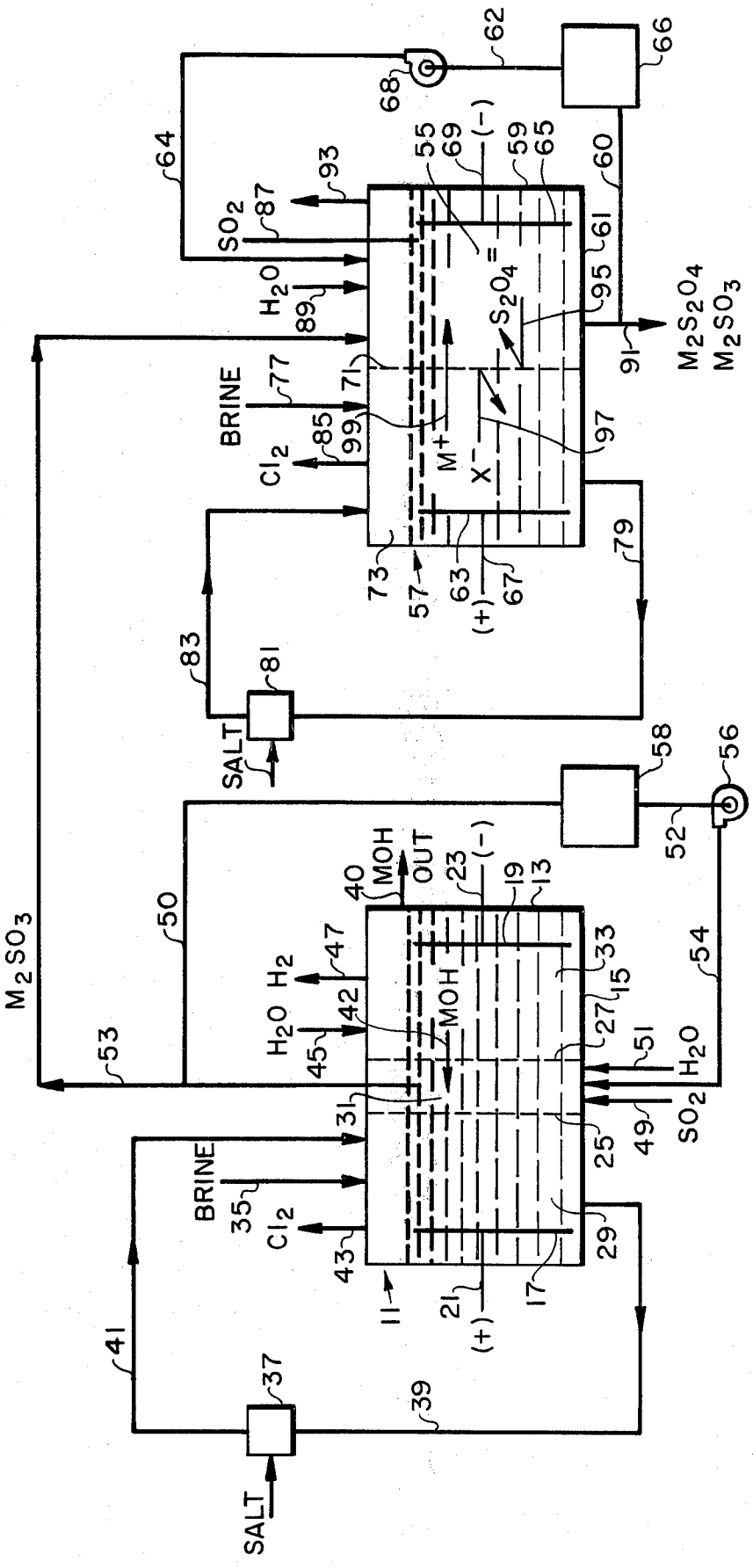
Primary Examiner—F. C. Edmundson
Attorney, Agent, or Firm—Peter F. Casella

[57] **ABSTRACT**

Dithionites are made by a process which begins with the production of high concentration, chloride-free sodium hydroxide solution and chlorine at a high current efficiency from a three-compartment electrolytic cell having membranes of a cation-active permselective membrane material separating anode and cathode compartments from a buffer compartment. Hydroxide ions migrating into the buffer compartment from the cathode compartment are converted to sulfite by reaction with sulfur dioxide, improving the current efficiency of the three-compartment cell, and the sulfite is removed. Subsequently, the sulfite resulting and additional sulfur dioxide are fed to the cathode compartment of a two-compartment electrolytic cell wherein the anode and cathode compartments are separated by a cation-active permselective membrane and in which chloride solution is being electrolyzed to chlorine at the anode and sulfite solution is being electrolyzed to dithionite at the cathode.

12 Claims, 1 Drawing Figure




SALT
BRINE
Cl_2
H_2O
SO_2
M_2SO_3
MOH
OUT
H_2
$M_2S_2O_4$
M_2SO_3
$S_2O_4^=$
M^+
X^-
(+)
(-)

ELECTROLYTIC MANUFACTURE OF DITHIONITES

This invention relates to the electrolytic manufacture of dithionites. More specifically, it is of a process for making alkali metal dithionite from alkali metal chloride and sulfur dioxide, utilizing a combination of electrolytic cells, one having three compartments and the other having two compartments, the compartments of each being separated by a cation-active permselective membrane which, in the best embodiments of the invention, is of a hydrolyzed polymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluorovinyl ether or is a sulfostyrenated perfluorinated ethylene propylene polymer.

The cation-active membranes mentioned allow proportions of hydroxyl ion generated at the cathodes of the cells to migrate to the buffer compartments of the three-compartment cells and to the anode compartments of the two-compartment cells. In the former case this portion of the hydroxyl generated is reacted with sulfur dioxide to produce sulfite and in the latter case may be converted to oxygen, thereby interfering with the efficiency of the two-compartment cell portion of the process. However, the proportion of hydroxide entering the anode compartment of the two-compartment cell is very low because it is consumed in the catholyte of that cell by reaction with sulfur dioxide therein to form larger anions, such as sulfite and dithionite, which do not readily penetrate the cation-active permselective membrane. Thus, dithionite and sulfite ions are prevented from migrating from the catholyte or buffer solution to the buffer solution or anolyte, chloride is prevented from migrating from the anolyte to the buffer or catholyte compartments and hydroxyl ion is effectively prevented from passing into the anolytes.

Dithionites and in particular, alkali metal dithionites, especially sodium dithionite, are useful bleaching agents and have been found to brighten or bleach wood pulps appreciably. Such a brightening or bleaching operation is an essential portion of many papermaking processes. Usually, the dithionite employed in the past has been zinc dithionite but to prevent water pollution the discharging of zinc ions into streams has been limited. Therefore, it has been found desirable to utilize other dithionites which are less objectionable. It has been suggested that dithionites could be made by the electrolysis of acidic solutions of sulfer dioxide, utilizing separating permselective membranes between anode and cathode compartments. Such a process has been described in Pulp and Paper Magazine of Canada, in the issue of Dec. 19, 1969, at pages 73–78. Such methods are feasible to some extent but the process of the present invention is far superior. It electrolytically produces hydroxide employed to make sulfite reactant, manufactures useful chlorine simultaneously, rather than useless oxygen, and makes a hydroxide and the bleaching product, both of which are low in chloride content. Such low chloride contents are advantageous since the proportion of chloride which may be discharged into streams and ground water is also limited. Although sulfite accompanies the dithionite, it may be usefully employed with it and is useful in making white liquor, utilized in papermaking processes. A special advantage of the present invention is in the utilization of the various products of the process in industrial plants, such as papermaking plants. The chloride-free hydroxide, dithionite, sulfite and chlorine are all useful products for papermaking and are produced in usable forms, without objectionable contaminants. They are made from a limited number of starting materials, primarily sources of chloride, e.g., salt, and sulfer dioxide, which may be obtained from the burning of sulfur or sulfur-containing ores.

In accordance with the present invention a method for electrolytically manufacturing a dithionite, chlorine, hydroxide and a sulfite from sulfur dioxide and a chloride comprises feeding chloride solution to the anode compartment of an electrolytic cell having anode, buffer and cathode compartments separated by cation-active permselective membranes, an anode in the anode compartment and a cathode in the cathode compartment and feeding sulfer dioxide to the buffer compartment, withdrawing chlorine from the anode compartment, hydroxide from the cathode compartment and sulfite from the buffer compartment, feeding such sulfite and sulfer dioxide to the cathode compartment of a two-compartment electrolytic cell having an anode in an anode compartment, a cathode in a cathode compartment and a cation-active permselective membrane dividing the compartments, feeding chloride to the anode compartment thereof and withdrawing chlorine from the anode compartment and dithionite and sulfite from the cathode compartment. Important advantages of this process include the manufacture of chloride-free, high concentration caustic in the three-compartment cell at a high current efficiency, together with useful chlorine from both cells, and the production of sodium dithionite in the cathode compartment of the two-compartment cell at a pH which is about neutral, preferably about 6 to 8, in which range the dithionite is comparatively stable, so that it may be used commercially as the aqueous solution produced, with sulfite, for the bleaching of wood pulp and other analogous processes.

The invention will be readily understood by reference to the following description of an embodiment thereof, taken in conjunction with the drawing of apparatuses utilized in carrying out the inventive process.

In the drawing:

The FIGURE is a schematic representation of a pair of electrolytic cells and auxiliary equipment for producing dithionite by the method of this invention.

In electrolytic cell **11**, outer wall **13** and bottom **15** enclose anode **17**, cathode **19** and conductive means **21** and **23**, respectively, for connecting the anode and cathode to sources of positive and negative electrical potentials, respectively. Cation-active permselective membranes **25** and **27** divide the cell volume into anode or anolyte compartment **29**, buffer compartment **31** and cathode or catholyte compartment **33**. An acidic aqueous solution of a halide or brine is indicated as passing into the anode compartment through line **35**. Such brine is used for initial charging of the anolyte and for make-up feed, although make-up may also be added before recirculated anolyte is admitted to the resaturator, to be described. Also, it may be desirable to dispense with brine line **35** and charge the cell initially and feed make-up through the resaturator piping. The chloride solution for the anolyte compartment, which may be maintained at a desired acidity by additions of acid, e.g., HCl, by conventional means, not shown, is circulated from the anode compartment through resaturator **37** via line **39** and exits from the resaturator through

line 41, from whence it returns to the anode compartment. In a normal operation, utilizing sodium chloride solution or other alkali metal chloride, the anolyte compartment is charged with a suitable chloride, e.g., a 25% salt solution, and that withdrawn for resaturation is at a lower concentration, e.g., about 22% NaCl. Chlorine, generated in the anode compartment by electrolysis of the halide solution, is taken off through line 43.

Water may be added to the cathode compartment 33 through piping 45 to maintain the desired level thereof and of the buffer compartment. Hydrogen is removed from this compartment through venting means 47. The buffer compartment has sulfur dioxide and water added to it through lines 49 and 51, respectively, and alkaline sodium sulfite is taken off through piping 53, through which it is transmitted to cathode compartment 55 of two-compartment electrolytic cell 57.

To increase circulation in the buffer compartment, effectively increase the volume of the compartment and to allow greater reaction times between the caustic and sulfur dioxide there may be provided a recirculation loop, for the buffer compartment including lines 50, 52 and 54, pump 56 and "holding tank" 58. The volume of such system may be 10 to 100,000 times that of the buffer compartment, preferably from 100 to 10,000 times such volume. High strength sodium hydroxide is removed from the cell through take-off piping 40, at a concentration of about 20 to 30% hydroxide, as sodium hydroxide, in water, and with a low chloride content, usually less than one gram per liter of NaCl. Some of the hydroxide produced in the cathode compartment 33 penetrates the cation-active permselective membrane 27 and passes into buffer compartment 31, wherein it reacts with the sulfur dioxide to produce sodium sulfite. The passage of the hydroxide into the buffer compartment is represented by arrow 42. Bacause of the reaction of the hydroxide in the buffer compartment and because the sulfite ion and SO_2 do not penetrate the membrane 25, very little hydroxide passes into the anode compartment 29 and therefore, the chlorine efficiency is maintained high. Also, of course, chloride ion does not pass from the anolyte into the buffer compartment, due to the repulsive effect of the permselective membrane. Additionally, the membranes and buffer zone prevent hydrogen or other cathode-produced gases from being mixed with chlorine, preventing the production of combustible gas mixtures.

Two-compartment cell 57 has sides 59 and bottom 61 enclosing anode 63 and cathode 65, which are connected to sources of positive and negative electrical potentials, respectively, through conductive means 67 anad 69. Cation-active permselective membrane 71 divides the two-compartment cell volume into anode or anolyte compartment 73 and cathode or catholyte compartment 55. Acidic aqueous halide, e.g., chloride solution or brine passes into the anode compartment through line 77 for initial charging of the anolyte and, if desired, for make-up feed. The halide or chloride solution for the anolyte compartment, also maintained at desired acidity in the same manner described for the three-compartment cell, is taken off from the anode compartment through line 79 and passes through resaturator 81, exiting through line 83 and returning to the anode compartment. Concentrations of chloride solution taken off and returned to that compartment are about the same as with respect to the three-compartment cell, already described. As with the three-compartment cell operation the use of the separate brine line may be discontinued in favor of utilization of the resaturator elements instead, to feed brine and make-up for any losses thereof. Also, instead of separate resaturators and attendant lines a single resaturator and appropriate piping may be used to maintain halide concentrations in both cell anolytes. Chlorine generated in the anode compartment of the two-compartment cell is removed therefrom through piping 85.

Cathode compartment 55 is charged with gaseous sulfur dioxide through line 87 and water is added through line 89. A mixture of dithionite and sulfite is removed via piping 91 and any hydrogen or other gases which may be produced in the cathode compartment are vented off via venting means 93. Analogously to the buffer solution recirculation in the three-compartment cell, catholyte of the two-compartment cell may also be recirculated, utilizing lines 60, 62 and 64, tank 66 and pump 68. The ratio of the total circulating system volume to that of the cathode compartment may be from 2:1 to 100,000:1 and is preferably 100:1 to 10,000:1.

During operations of the cells high concentration, low chloride caustic is taken off from the three-compartment cell and is ready for use in wood pulping, bleaching or other operations and chlorine removed from the anode compartment of the three-compartment cell is useful in the bleaching of wood pulp or for other pulp and paper mills' industrial purposes. The sulfite, produced in alkaline form due to the content of hydroxide therein, is converted in the two-compartment cell to dithionite and additional sulfite is made by reaction of sulfur dioxide with hydroxide generated in the cathode compartment. As is clear from the diagram, the two-compartment cell also makes chlorine, useful in pulp bleaching. The sulfite made by reaction of the sulfur dioxide with hydroxide in the cathode compartment is useful in pulping operations and may be converted to white liquor after completion of bleaching of pulp by the accompanying dithionite. The sulfur dioxide performs the important function of regulating the pH in the cathode compartment of the two-compartment cell so as to maintain it in the range of 6 to 8, thereby stabilizing the dithionite produced. Although the mechanism of the reaction has been described, applicants should not be considered as being bound by this description, since it may also be theorized that the sulfur dioxide charged is reduced to dithionic acid, which is then neutralized by hydroxyl present to form dithionite. In such case, the presence of the sulfite can help to exert a buffering effect to maintain the desired pH.

As is illustrated schematically by arrow 95 the dithionite (and sulfite) ions do not penetrate the permselective membrane 71 and therefore, are held in the cathode compartment 55. Similarly, halide ions, the path of which is indicated by an arrow identified by numeral 97, do not pass from the anolyte to the catholyte of the two-compartment cell. However, cations such as alkali metal ions, e.g., Na^+, indicated by M^+ in the illustration, the direction of which is represented by the arrow 99 headed toward the right on the right side of the drawing, may pass from anolyte to catholyte. A small proportion of hydroxyl ion may penetrate the membrane 71 but usually the concentration of free hydroxyl

is low in the catholyte, due to reaction with sulfur dioxide and reduction of the pH to the 6 to 8 range, so that the hydroxyl entering the anolyte, if any, has little effect on chloride current efficiency.

By the described process, utilizing a combination of three-compartment and two-compartment cells, the sulfur dioxide feed to the buffer compartment of the three-compartment cell ties up the sodium hydroxide penetrating the membrane between the catholyte and buffer solution and prevents it from reaching the anode, where it could be converted to useless oxygen, thereby decreasing current efficiency. At the same time, high strength, chloride-free caustic is made, which is important in various chemical operations, e.g., pulp bleaching, where chloride discharges from industrial plants are undesirable and may be strictly limited.

The chlorine and chloride-free caustic made are both useful chemicals for many industrial processes, including wood pulping and pulp bleaching. Thus, the invention has a distinct advantage over an electrolytic method for producing dithionite by charging sulfite or sulfur dioxide to a two-compartment cell and producing dithionite in the cathode compartment reduction of sulfite or reduction of sulfur dioxide, followed by neutralization to the dithionite. That is, the sulfur dioxide which would be required to make sulfite for the two-compartment cell electrolytic reaction, makes the sulfite in the buffer compartment of the three-compartment cell while chloride-free caustic is made in the cathode compartment, and increases chlorine current efficiency of the cell. These additional advantages improve the efficiency of the present process and make it commerically advantageous over similar or related processes.

Instead of adding sulfur dioxide to the cathode compartment, wherein it acts as a source of sulfite for reduction to dithionite and at the same time serves to help regulate the pH in the desired 6 and 8 range, sulfite may be fed to the catholyte, with other means employed for pH regulation. By such a process, although the results may not be as satisfactory as with that previously described, utilizing sulfur dioxide, dithionite can be made. However, unless the means of reducing the alkaline pH caused by the presence of the hydroxide generated at the cathode is a chemical which produces a useful prduct (and which is non-interfering with the dithionite process), there will be a waste of hydroxide and possibly, even creation of a disposal problem.

The halide solution fed to the anode compartment of both cells is an aqueous solution of a water soluble metal chloride in the usual case, preferably of sodium chloride. The concentration thereof is generally in the range of 200 to 320 grams/liter for sodium chloride and 200 to 360 g./l. for potassium chloride. preferably such solutions contain 20 to 25% of the alkali metal halide salt, as the solutions are charged to the cell or delivered to it from the resaturator. Generally the chloride content will be reduced to 5 to 30% less than the original content, preferably to 10 to 20% less and normally, as with sodium chloride, the concentration of the halide removed from the anode compartment for resaturation and return to such compartment is about 22 %, as NaCl, or equivalent. Although the anolyte may be neutral, it is often acidified so as to be of a pH in the range of about 1 to 6, preferably 2 to 4, with acidification normally being effected with a suitable acid, such as hydrochloric acid. Water utilized to make the initial brine charge or added as make-up feed to the anode compartments and water added to the other compartments of the cells will preferably be deionized, containing less than 10 p.p.m. hardness, as $CaCO_3$, although tap water of comparatively low hardness, e.g., under 150 p.p.m., preferably under 50 p.p.m., can be used.

The sulfur dioxide charged to the buffer compartment of the three-compartment cell is usually substantially pure e.g., over 90% SO_2, but lower concentrations thereof, e.g., as low as 20%, are usable because of the desirable attributes of the membrane material in preventing gas interchanges between cell portions. Thus, the unreacted gas, e.g., O_2, N_2, may be removed from line 53 at a suitable point, before the sulfite produced is charged to the cathode compartment of the two-compartment cell.

In the three-compartment cell high concentration hydroxide solution, such as alkali metal hydroxide, preferably sodium hydroxide, is produced, normally of 20 to 30% hydroxide, although lesser concentrations may also be made, e.g., down to as low as 5%. The chloride content thereof is low, usually being less than 5 g./l. and often less than 1 g./l. The concentration of the hydroxide may be regulated by controls of the rate of feed of water to the catholyte, flow of electric current and, in some cases, nature of the feed to the cathode compartment (dilute caustic may sometimes be fed in at least partial replacement of water).

The sulfite produced by reaction of the sodium hydroxide and sulfur dioxide in the buffer compartment may be of any of various concentrations. These are controllable by regulating the feed of sulfur dioxide to the buffer compartment. The more sulfur dioxide charged, the greater the quantity of sulfite in the buffer effluent, in comparison to that of the hydroxide. Generally, the sulfite will be an aqueous solution of 1 to 15% strength and the hydroxide removed fro the buffer compartment will also be a corresponding 15 to 1% solution, with more sulfite than hydroxide in the buffer compartment. Preferably the sulfite and hydroxide concentrations total about 10 to 20%, e.g., about 15%, and in more preferred embodiments of the invention the concentration of hydroxide is maintained at less than 5% while that of the sulfite is up to about 10%.

In the two-compartment cell the feeds to the catholyte of sulfite-hydroxide solution from the buffer compartment and SO_2 are so regulated as to maintain the desired pH for the formation of a stable dithionite. Such a pH should be in the range of about 6 to 8, preferably 6 to 8 and most preferably about 7. It may be regulated by controlling the feed of sulfur dioxide, which has the additional beneficial effect of diminishing the hydroxide concentration to a very small proportion, preventing all but a very minor proportion of the hydroxide generated at the cathode from migrating through the membrane to the anolyte, where it could have been converted to oxygen, with a loss of electrical efficiency. The effluent from the cathode compartment is a mixture of dithionite and sulfite and the concentrations of these components are usually in the ranges of 0.5 to 30% sulfite and 0.5 to 10% dithionite. Within such ranges the normal ranges are from 10 to 20% of sulfite and 1 and 5% of dithionite. The conversion of sulfite or sulfur dioxide to dithionite will usually be at a current efficiency of from about 40 to 80%, normally within the 60 to 75% range. The dithionite removed from the cathode compartment of the two-

compartment cell will generally have a concentration of 10 to 70 g./l., within which range 30 to 50 g./l. is usual. From 100 to 250 g./l. will be the concentration of the sulfite drawn off with it.

To obtain the desired operation of these cells, as described, the voltage drop across the three-compartment cell is maintained at about 3 to 6 volts, preferably 4 to 5 volts and that across the two-compartment cell is about 3 to 5 volts, preferably 3.5 to 4.5 volts. The current density for the three-compartment cell is about 1 to 3 amperes/sq. in., preferably 1.5 to 2.5 a.s.i., and that of the two-compartment cell is 0.1 to 2 a.s.i., preferably 0.2 to 1 a.s.i. The operating temperature of the three-compartment cell is about 50° to 100°C., preferably 80° to 100°C., whereas that of the two-compartment cell is 3° to 40°C., preferably 3° to 25°C. A low temperature is desirable for operation of the two-compartment cell because of the greater stability of the dithionite at such low temperatures.

The anodes employed are preferably dimensionally stable anodes of a material selected from the group consisting of noble metals, noble metal alloys, noble metal oxides, mixtures of noble metal oxides with valve metal oxides and mixtures thereof, on a valve metal, whereas the cathodes are preferably of stainless steel. Instead of the dimensionally stable anodes, anodes of noble metals or oxides thereof may also be employed, e.g., platinum, iridium, ruthenium or rhodium. Alternatively, other anodes resistant to the anolytes can be used, although they are not usually preferred. The anodes and cathodes may be connected to sources of electrical potential by conductive metals, such as copper, silver, aluminum, steel and iron but these materials are normally shielded from contact with the electrolytes. Preferable dimensionally stable anode surfaces, all on titanium or tantalum substrates, are ruthenium oxide-titanium oxide mixtures, platinum, ruthenium, platinum oxide and mixtures of ruthenium and platinum and mixtures of their oxides. A preferred dimensionally stable anode is a ruthenium oxide-titanium dioxide mixture on a titanium substrate, connected to a source of positive electrical potential by a titanium-clad copper conductor.

The cathodes employed should be resistant to the corrosive catholyte and therefore it had been found that noble metal, noble metal oxide and stainless steel cathodes are preferred. Ordinary iron or steel cathodes soon become deteriorated in use, although they may be employed for short term operations. Graphite cathodes are not preferred because of their poorer conductivity and other physical properties. Of the noble metals, those previously described are satisfactory and of the stainless steels those containing small proportions of molybdenum, in addition to chromium, nickel and iron, are preferred. These include Stainless Steel Types Nos. 316 to 317. However, other stainless steels of high resistances to corrosion by the catholyte environments may also be employed, many of which may contain about 18% of chromium and 8% of nickel. The various stainless steels from which corrosion-resistant anodes may be made are described in Section 24 of the Steel Products Manual, issued by the American Iron and Steel Institute in February, 1949, under the heading "Stainless and Heat-Resisting Steels". A summary of such steel formulations and corresponding type numbers is found in the Handbook of Engineering Fundamentals by Eshback, Second Edition, published in 1952 by John Wiley & Sons, Inc., New York, page 12–40 and discussions of such steels and their corrosion resistances is at page 12–39. In addition to the stainless steels, other corrosion resistant steels such as silicon steels, nickel steels, and other conductivve materials resistant to corrosion may also be employed as cathode materials or surfaces.

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 anad 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 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 hydro-

lysis, 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 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 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 commerical 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 electrochemical cell operations.

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 patent publication No. **2,152,194**, 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 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 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 **16ST12S**, the former being **18%** styrenated and having two-thirds of the phenyl groups monosulfonated and the latter being **16%** styrenated and having thirteen-sixteenths 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 thickness greater than that of the film may also be successfully employed, e.g., **1.1** to five 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 processes of this invention obtain good current efficiencies for the manufacture of chlorine and acceptable current efficiencies for producing hydroxide, sulfite and dithionite. In preferred embodiments of the invention, when sodium chloride is utilized and sodium sulfite and sodium dithionite are made, the current efficiencies for the productions of chlorine in both cells are from **90** to **99%**, usually being **94** to **97%**, e.g., **96%**. The production of caustic in the three-compartment cell, including caustic produced in the cathode compartment, whether removed therefrom the buffer compartment and whether removed from the buffer compartment as caustic or sulfite, is at a current efficiency or sodium ion efficiency of about **70** or **75** or **90%**. Approximately **5** to **50%** of the hydroxide produced in the cathode compartment migrates to the buffer compartment and usually this will be from **5** to **25%**. In the two-compartment cell the current efficiency for the production of the dithionite will normally be from **40** to **80%**, usually **60** to **75%**, with the conversion of sulfur dioxide or sulfite to dithionite being about **20** to **50%**. such efficiencies are acceptable and although the efficiency for the manufacture of dithionite might appear low, considering that useful sulfite is also made, it is satisfactory.

The present cells may be incorporated in large or small electrochemical plants, those producing bleaching dithionite and accompanying sulfite while also making from **20** to **1,000** tons per day of chlorine or equivalent derivative. In all cases the efficiencies obtainable are such as to make the processes economically desirable. It is highly preferred, however, that the installation should be located near to and should be used in conjunction with a groundwood or woodpulp bleaching plant so that the dithionite produced can be employed promptly as a bleach and the other chemicals may also be used for pulping or bleaching purposes without the need to ship them long distances to ultimate consumers. Of course, if desired, the chlorine and caustic may be so shipped or may be chemically converted to other materials. In some instances the chlorine may be liquefied and the caustic may be evaporated to a higher concentration so as to facilitate shipment or transfer.

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

Utilizing the apparatus illustrated in the FIGURE, useful sodium dithionite in aqueous solution, accompanied by sodium sulfite, is produced and is successfully employed in the bleaching of groundwood pulp.

The materials of construction of the three-compartment and two-compartment cells include as a preferred material, asbestos filled polypropylene. I anodes are dimensionally stable anodes of titanium having ruthenium-titanium oxide coatings. The titanium mesh-based anodes are connected to sources of electricity by titanium-clad copper rods. The cathodes are of Type **316** stainless steel. In other experiments, yielding essentially the same results, the internal cell walls are of such materials as chlorinated polyethylene or chlorinated polypropylene, the anodes are of platinum or platinum-iridium alloy and the cathodes are of Type **317** stainless steel.

The cation-active permselective membranes employed have a wall thickness of **7** mils (about **0.2** mm.) and the membrane portion thereof is joined to a backing or supporting network of polytetrafluoroethylene (Teflon) filaments having a diameter of about **0.1** mm. and woven into cloth form such that the area percentage of openings therein is of 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 portions of the membranes actually flowing around the filaments during the fusion processes to lock onto the cloth. The described permselective membranes are obtainable from E. I. Du Pont de Nemours and Company, Inc., Plastics Department, Wilmington, Del. **19898,** as XR Perfluorosulfonic Acid Membranes. The material thereof 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 **1,100** to **1,400** range, about **1,250.**

Although in the FIGURE, for clarity of presentation, sides of the membranes the electrodes are apart from the membranes, in the practice of the present process the electrodes are in contact with the membranes in the three-compartment cell, with the "flatter"sides of the membranes facing the contacting electrodes. In the three-compartment cell the buffer compartment volume is about **10%** of the total of the anode and cathode compartment volumes, which are of about the same volume. In the two-compartment cell, cell volumes are about equal and the electrodes are about one-forth inch or **6.3** mm. apart.

The feeds to the anode compartments of both cells are **25%** sodium chloride solutions in water and the depleted anolytes in both cases are at **22%** sodium chloride contents with circulations of the depleted anolytes through the resaturators (or a single resaturator) being controlled by sensors, valves and pumps to maintain this desired difference in concentration between feed and take-off solutions to/from the anode compartment.

In the case of the three-compartment cell the feed of sulfur dioxide to the buffer compartment is regulated so as to produce an effluent from that compartment comprising about **10%** of sodium sulfite and **10 %** of sodium hydroxide in water. Water feed to the buffer compart-

ment and water feed and caustic producing conditions in the cathode compartment may also be regulated to adjust the proportion of sulfite to hydroxide leaving the buffer compartment. The pH of such solution is that the caustic, **14.** Under best operating conditions of the three-compartment cell the proportion of hydroxide passing from the cathode compartment to the buffer compartment is or averages about **25%** of that produced at the cathode and this ratio is in the range of **5** to **50%**. The high concentration, low chloride content hydroxide taken off from the cathode compartment is a **25%** hydroxide and has a chloride content of about **0.05%**. The temperature of the electrolyte is maintained at about **90°C.** during the process, with **4.5** volts impressed across the electrodes and a current density of **2** a.s.i., the current flow being **90** kiloamperes.

In the two-compartment cell the feed to the catholyte is the effluent from the buffer compartment of a three-compartment cell and preferably it is cooled en route by cooling means, not illustrated in the drawing, so as to enter the cathode compartment of the two-compartment cell at the desired cell temperature, about **20°C.** (within a range of **15°** to **35°C.**). sulfur dioxide is added to the cathode compartment at such a rate as to maintain the pH of the catholyte at **7,** although it may vary between **6** and **8.** Under flow rates described, about **60%** of the cathodic current is utilized in the production of dithionite and about **40%** to make sulfite from hydroxide and sulfur dioxide. The effluent from the cathode compartment is an aqueous solution containing **16%** of sodium sulfite and **3.7%** of sodium dithionite.

The installation described produces **0.36** ton per day of sodium dithionite, in a **3.7%** concentration aqueous solution, with **33%** conversion of sulfur dioxide to dithionite and with the dithionite obtained at **75** percent current efficiency, calculated on the basis of useful products obtained. The chlorine produced from the two-compartment cell is at the rate of **0.3** ton per day and the current efficiency is **95%**. With respect with the three-compartment cell, the chlorine production is at the rate of **3** tons per day, also with a **95%** current efficiency. The sodium hydroxide taken of the cathode compartment of the three-compartment cell is produced at the rate of **2.28** tons per day and is in **25%** aqueous solution. The sulfur dioxide feed to the buffer compartment cell is **0.49** ton per day with production of sodium sulfite from that compartment being at **0.97** ton per day and with **0.39** ton per day of sodium hydroxide accompanying it. Current efficiency for the production of sulfite and hydroxide in the three-compartment cell, or sodium ion efficiency, is about **90%**.

The solution of dithionite and sodium sulfite from the cathode compartment of the two-compartment cell is continuously employed to bleach groundwood pulp, after dilution to a **1%** dithionite solution. The groundwood charge is an **85:15** mixture of West Coast hemlock and balsam, the rate of application is **1.1** percent of sodium dithionite, on a dry pulp basis and the pulp is in a **3** percent aqueous slurry buffered to a pH of about **6.5** with potassium hydrogen phosphate before addition of the dithionite. A brightness increase of about **10** units is obtained at a brightening temperature of **60°–70°C.** after about **30** minutes treatment. Reversion in such cases is about **2** units.

The bleach liquor is recovered and mixed with black liquor which is subsequently converted to white liquor used in pulping.

EXAMPLE 2

The procedure of Example **1** is followed except for the addition of sulfur dioxide to the catholyte of the two-compartment cell. Instead of the sulfur dioxide, additional sulfite is added and the desired pH of **7** is maintained in the cathode compartment by continuous addition of sulfuric acid, sodium bisulfate, sodium bisulfite or any other suitable acidic or alkaline neutralizing agent or buffer. Although the current efficiency is not as good as in the processes utilizing a sulfur dioxide feed to the catholyte of the two-compartment cell, the process is operative and production of dithionite and other product is at essentially the same rate as previously described. The dithionite solution obtained is effective for groundwood bleaching, as described in Example **1,** and is useful for other bleaching purposes, too.

In variations of this process and that of Example **1** the sulfur dioxide is fed to the buffer compartment of the three-compartment cell and to the cathode compartment of the two-compartment cell as aqueous solutions containing about **8%** of sulfur dioxide. Utilizing the solutions fewer problems of gas bubbling and interference with electrode reactions are experienced but weaker product is obtained. In other modifications of the experiments, batch and continuous processes are employed. The continuous processes, sometimes with recycles of each of the compartment contents, are generally superior, yielding a more consistent product and readily lending themselves to automatic control.

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 of electrolytically manufacturing a dithionite, chlorine, a hydroxide and a sulfite from sulfur dioxide and a chloride which comprises feeding chloride solution to the anode compartment of an electrolytic cell having anode, buffer and cathode compartments separated by cation-active permselective membranes, an anode in the anode compartment and a cathode in the cathode compartment, and feeding sulfur dioxide to the buffer compartment, withdrawing chlorine from the anode compartment, hydroxide from the cathode compartment and sulfite from the buffer compartment, feeding such sulfite and sulfur dioxide to the cathode compartment of a two-compartment electrolytic cell having an anode in an anode compartment, a cathode in a cathode compartment and a cation-active permselective membrane dividing the compartments, maintaining the catholyte at pH **6–8,** feeding chloride to the anode compartment thereof and withdrawing chlorine from the anode compartment and dithionite and sulfite from the cathode compartment.

2. A method according to claim **1** wherein the material of the cation-active permselective membranes is selected from the group consisting of a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluro-sulfonated perfluovinyl ether, and a sulfostyrenated perflourinated ethylene propylene polymer, and the

cells employed are three- and two-compartment cells.

3. A method according to claim 2 wherein the permselective membrane is of a hydrolyzed copolymer of tetrafluoroethylene and $FSO_2CF_2CF_2OCF(CF_3)CF_2OCF''CF_2$, which copolymer has an equivalent weight of about 900 to 1,600.

4. A method according to claim 3 wherein the voltage drop across the three-compartment cell is about 3 to 6 volts, that across the two-compartment cell is about 3 to 5 volts, the current density for the three-compartment cell is about 1 to 3 amperes/sq. in., that for the two-compartment cell is about 0.1 to 2 amperes/sq. in. and the operating temperature of the three-compartment cell is about 50° to 100°C. and that of the two-compartment cell is about 3° to 40°C.

5. A method according to claim 4 wherein the membrane walls are from about 0.02 to about 0.5 mm. thick, the membranes are mounted on a network screen or cloth of filaments of a material selected from the group consisting of polytetrafluroethylene, perfluorinated ethylene propylene polymer, polyproplyene, titanium, tantalum, niobium and noble metals, which has an area percentage of openings therein from about 8 to about 80% with the filaments having a thickness of about 0.01 to about 0.5 mm.

6. A method according to claim 5 wherein the voltage drop across the three compartment cell is from 4 to 5 volts, that across the two-compartment cell is from 3.5 to 4.5 volts, the current density in the three-compartment cell is from 3.5 to 4.5 volts, the current density in the three-compartment cell is from about 1.5 to 2.5 amperes/sq. in., the current density in the two-compartments cell is 0.2 to 1 amperes/sq. in., the current density in the two-compartment cell is 0.2 to 1 ampere/sq. in., the operating temperature of the three-compartment cell if 80° to 100°C., the operating temperature of the two-compartment cell is 3° to 25°C., the feed to the anode compartment of the three compartment cell is a chloride solution containing 20 to 25% of chloride, the hydroxide removed from the cathode compartment of that cell is an aqueous solution at a concentration of 20 to 30% hydroxide, the sulfite withdrawn from the buffer compartment of the same cell is an aqueous solution at a concentration of 1 to 15% sulfite and accompanying it is sodium hydroxide, at a concentration of 15 to 1% hydroxide, the chloride feed to the anolyte compartment of the two-compartment cell is essentially the same as that of the feed of such compartment of the three-compartment cell, and the dithionite and sulfite removed from the catholyte compartment of the two-compartment cell are in aqueous solution at a concentration of 10 to 70 g./l. of the dithionite and 100 to 250 g./l. of the sulfite.

7. A method according to claim 6 wherein the anodes are dimensionally stable anodes of material selected from the group consisting of noble metals, noble metal alloys, noble metal oxides, mixtures of noble metal oxides with valve metal oxides, and mixtures thereof, on a valve metal, and the cathode is stainless steel.

8. A method according to claim 7 wherein the chloride is sodium chloride, the hydroxide is sodium hydroxide, the sulfite is sodium sulfite and the dithionite produced is sodium dithionite, the anolytes are recirculated and the depleted anolytes are increased in concentration to about 25% NaCl, at which concentration they are fed to the anode compartments, by dissolving solid sodium chloride therein.

9. A method according to claim 8 wherein the membrane copolymer equivalent weight is from 1,100 to 1,400, the membrane wall thickness is 0.1 to 0.3 mm., the anode is ruthenium oxide on titanium, the pH's of the anolytes are about 2 to 4 and the dithionite withdrawn is in an aqueous solution with sodium sulfite, wherein the dithionite concentration is from 30 to 50 g./l.

10. A method for electrolytically maunfacturing a dithionite, chlorine and a hydroxide from sulfur dioxide and a chloride which comprises feeding chloride solution to the anode compartment of an electrolytic cell having anode, buffer and cathode compartments separated by cation-active permselective membranes, an anode in the anode compartment and a cathode in the cathode compartment, and feeding sulfur dioxide to the buffer compartment, withdrawing chlorine from the anode compartment, hydroxide from the cathode compartment and sulfite from the buffer compartment, feeding such sulfite to the cathode compartment of a two-compartment electrolytic cell having an anode in an anode compartment, a cathode in a cathode compartment and a cation-active permselective membrane dividing the compartments, maintaining the pH in the cathode compartment of the two-compartment electrolytic cell at about 6 to 8, feeding chloride to the anode compartment of such cell and withdrawing chlorine from the anode compartment and dithionite from the cathode compartment.

11. A method according to claim 10 wherein the cation-active permselective membranes are selected from the group consisting of a hydrolyzed copolymer of a perfluorinated hydrocarbon and a fluorosulfonated perfluoroyinyl ether, and a sulfostyrenated perfluorinated ethylene propylene polymer, the wall thickness of the membranes is from about 0.02 to 0.05 mm. the hydroxide produced in the cathode compartment of the three-compartment cell is of a high concentration and chloride-free, the sulfite is of a concentration of 1 to 15%, the voltage drop across the three-compartment cell is about 3 to 6 volts, that across the two-compartment cell is about 3 to 5 volts, the current density for the three-compartment cell is about 1 to 3 amperes/sq. in., that for the two-compartment cell is about 0.1 to 2 amperes/sq. in. and the operating temperature of the three-compartment cell is about 50° to 100°C. and that of the two compartment cell is about 3° to 40°C.

12. A method according to claim 11 wherein the permselective membrane is of a hydrolyzed copolymer of tetrafluoroethylene and $FSO_2CF_2CF_2OCF(CF_3)CF_2OCF{=}CF_2$, which copolymer has an equivalent weight of of about 1,100 to 1,400, the membrane thickness is from 0.1 to 0.3 mm., the anodes are dimensionally stable anodes of material selected from the group consisting of noble metals, noble metal alloys, noble metal oxides, mixtures of noble metal oxides with valve metal oxides, and mixtures thereof, on a valve metal, the cathodes are stainless steel, the chloride, hydroxide, sulfite and dithionite are sodium salts, the sodium chloride is charged to the anode compartments of the cells in an aqueous solution at a concentration of about 20 to 25% NaCl and the dithionite produced is in aqueous solution at a concentration of 5 to 50 g./l.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,905,879

DATED : September 16, 1975

INVENTOR(S) : Jeffrey D. Eng and Cyril J. Harke

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

Column 3, line 38 change "Bacause" to ---Because---;
Column 5, line 47 change "prduct" to ---product---;
Column 6, line 38 change "fro" to ---from---;
Column 8, line 5, change "conductivve" to ---conductive---;
Column 10, line 26 change "16ST12S" to ---16ST13S---;
Column 12, line 41, "$CFCF_2$" to ---$CF=CF_2$---;
Column 15, line 4 change "$CFCF_2$" to ---$CF=CF_2$---;
Column 15, lines 29-30, delete "the current density in the three-compartment cell is from 3.5 to 4.5 volts,"
Column 15, lines 33-35, delete the second occurrence of the phrase "the current density in the two-compartment cell is 0.2 to 1 ampere/sq. in.,"
Column 16, line 10, change "maunfacturing" to ---manufacturing--

Signed and Sealed this

twenty-third Day of *December 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks