July 24, 1973 **A. H. HEIT ET AL** **3,748,238**

ELECTROLYTIC PROCESS FOR THE PREPARATION OF SODIUM HYDROSULFITE

Filed May 8, 1972 3 Sheets-Sheet 1

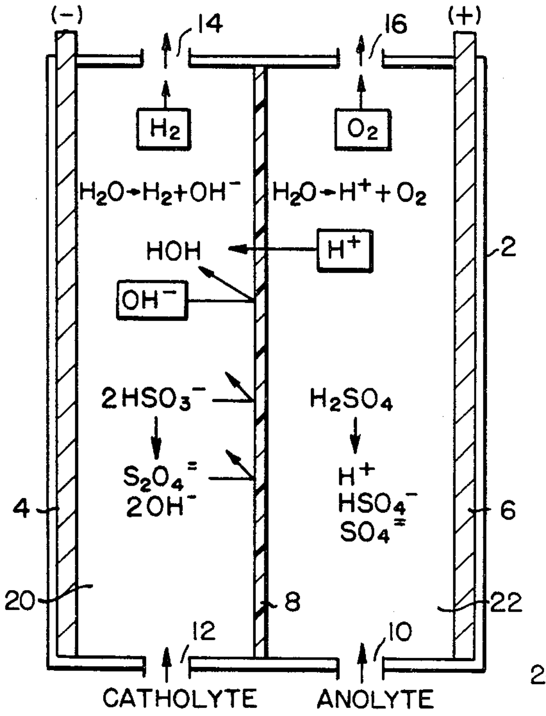


FIG. 1

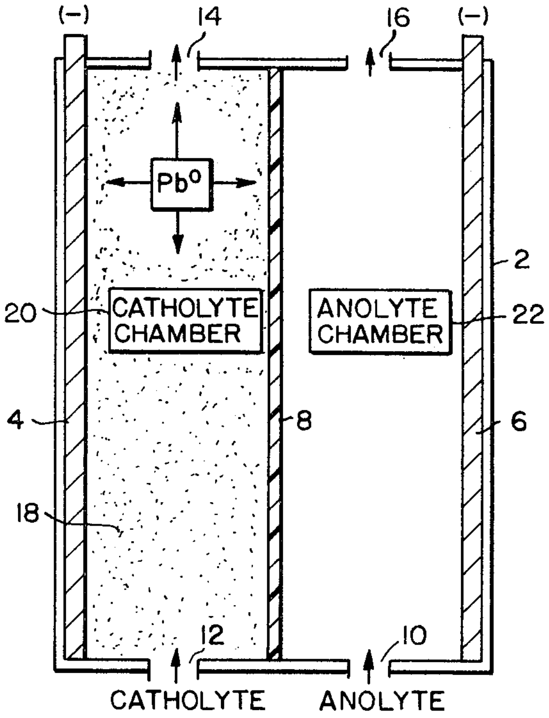


FIG. 3

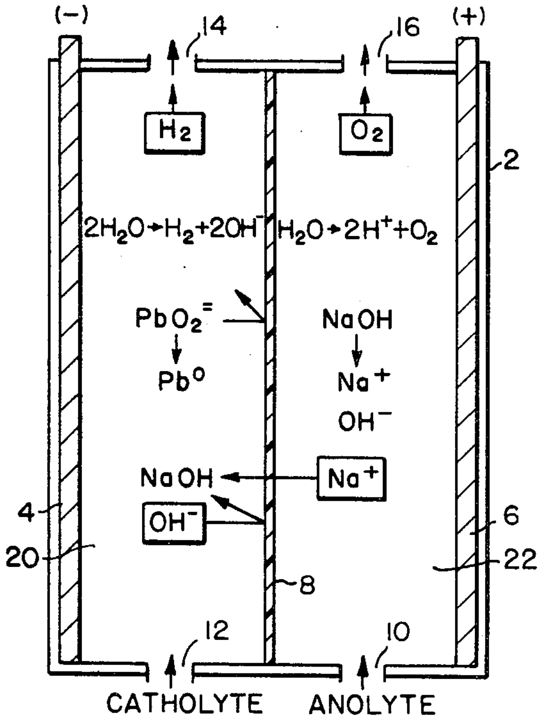


FIG. 2

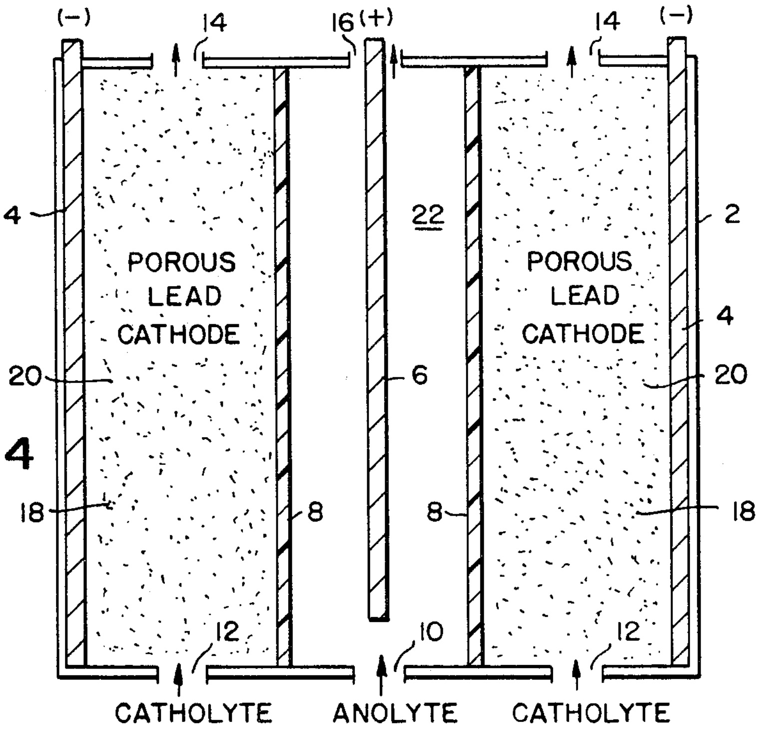
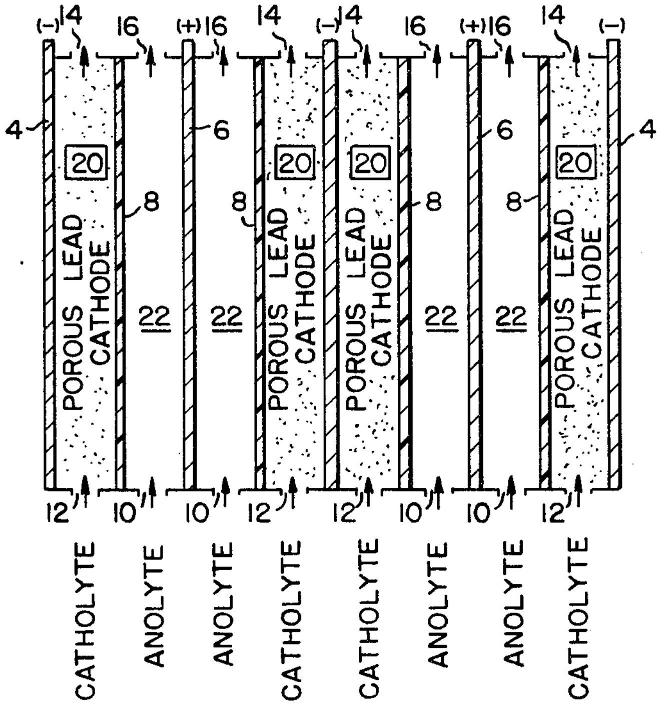

(−)
14
16 (+)
14
(−)
4
22
2
POROUS LEAD CATHODE
POROUS LEAD CATHODE
4
20
6
20
18
8
8
18
12
10
12
CATHOLYTE
ANOLYTE
CATHOLYTE

FIG. 4


(−) 14
16
(+) 16
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4
6
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20
20
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POROUS LEAD CATHODE
POROUS LEAD CATHODE
POROUS LEAD CATHODE
POROUS LEAD CATHODE
22
22
22
22
12
10
10
12
12
10
10
12
CATHOLYTE
ANOLYTE
ANOLYTE
CATHOLYTE
CATHOLYTE
ANOLYTE
ANOLYTE
CATHOLYTE

FIG. 5

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ELECTROLYTIC PROCESS FOR THE PREPARATION OF SODIUM HYDROSULFITE

Filed May 8, 1972 3 Sheets-Sheet 3

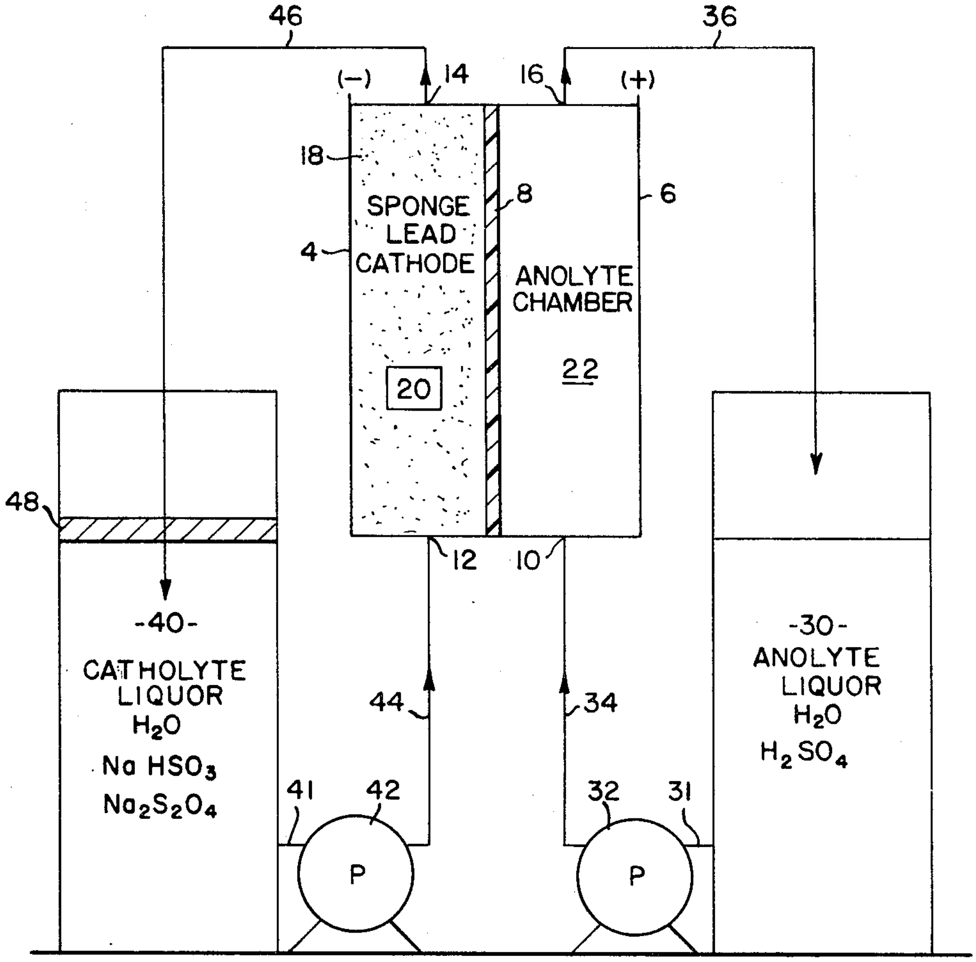

FIG. 6

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Patented July 24, 1973

3,748,238

ELECTROLYTIC PROCESS FOR THE PREPARATION OF SODIUM HYDROSULFITE

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Int. Cl. C01d *5/00;* C23b *5/16;* B01k *3/04*
U.S. Cl. 204—92 9 Claims

ABSTRACT OF THE DISCLOSURE

Sodium hydrosulfite is prepared from sodium bisulfite or sodium metabisulfite in an electrodialytic apparatus provided with a special spongy, porous lead electrode used therein as a cathode, which substantially fills the catholyte chamber of the apparatus. The spongy, porous lead electrode which makes the cathodic reduction of the bisulfite ion feasible in the electrodialytic apparatus, is produced from the alkali metal plumbities in an electrodialytic apparatus having an anode chamber and at least one cathode chamber adjacent the anode chamber with designated ion migrating means (membranes) positioned between the anode and cathode chambers. The bisulfite ion reduction to hydrosulfite anion is carried out in the same electrodialysis apparatus as, or an electrodialysis apparatus similar to, the apparatus used to produce the spongy, porous lead electrode.

BACKGROUND OF THE INVENTION

This invention relates generally to electrodialysis, and more particularly, to a method and apparatus for the electrodialytic preparation of hydrosulfites from bisulfites. It also relates to a new and novel electrode and to an electrodialytic method of producing an electrode from plumbite anion.

The hydrosulfites, a term which is interchangeable herein with the term dithionites, hydrosulfite salts or dithionite salts, have found great commercial use due to their powerful reducing action on many materials. The dithionites readily reduce several metal ions to the metal, disulfide linkages in wool and hair, many nitro compounds and many dyes. Principal applications are in various textile operations, such as dyeing, printing and stripping. Dithionites are also used for bleaching of ground wood pulp, soap, sugar, molasses and glue.

The ionic equation for the electrodialytic preparation of hydrosulfite ion from bisulfite ion is

$$2HSO_3^- \rightarrow S_2O_4^{-2} + 2OH^-$$

wherein HSO_3^- represents bisulfite ion and $S_2O_4^{-2}$ represents hydrosulfite ion. When the sodium salt is used, the chemical equation for the electrodialytic preparation of sodium hydrosulfite is

$$2NaHSO_3 \rightarrow Na_2S_2O_4 + H_2O$$

One chemical method for the production of sodium hydrosulfite is carried out in accordance with the following two equations where liquid sulfur dioxide is reacted with zinc dust slurried in water to produce zinc hydrosulfite which is converted to the sodium salt by means of caustic soda:

$$Zn + 2SO_2 \rightarrow ZnS_2O_4$$
$$ZnS_2O_4 + 2NaOH \rightarrow Zn(OH)_2 + Na_2S_2O_4$$

The zinc hydroxide and sodium dithionite (sodium hydrosulfite) slurry is filtered, washed, treated with sodium sulfide, salted out with salt and alcohol, dehydrated with direct steam, washed and vacuum dryed as disclosed in Kirk-Othmer "Encyclopedia of Chemical Technology," 19, 421 (1969). Further disclosed in the cited Kirk-Othmer reference is the electrolytic reduction of sodium bisulfite to sodium dithionite in a hydrogen atmosphere. The chemical method is characterized by an excessive number of steps which are uneconomical to carry out and which tend to expose the sodium dithionite, $Na_2S_2O_4$, to air and thereby cause rapid oxidation of the dithionite to the metabisulfite since the dihydrate is generally the form which crystallizes from solution and since the dihydrate rapidly oxidizes in air to the metabisulfite. In the prior art electrolytic method the preferred cathode is a mercury cathode which is continuously stirred (Patel et al., Proc. Natl. Inst. Sci. India 15, 131 (1949)). Although current efficiencies have been improved in those processes using the stirred mercury cathode, there are many drawbacks in utilizing such an electrode in continuous electrodialytic operations. For example, the mercury becomes dispersed in the liquor and may become distributed throughout the system from the continuous stirring and agitation. Furthermore, in cell construction of the type generally used for industrial application, it is difficult to confine mercury to form an electrode. Liquors passing through the chambers of electrodialytic cells would gradually sweep the mercury from the chamber. Hence, the mercury cathode used in the prior art is impractical in an electrodialytic apparatus used in processing large quantities of sodium bisulfite or sodium metabisulfite to form sodium hydrosulfite. Furthermore, since the prior art electrolytic method is carried out in a hydrogen atmosphere, there is increased hazard of explosion. The hydrosulfite or dithionite is thermally unstable, and the use of hydrogen, inherently explosive, increases the chance of thermal decomposition of the hydrosulfite, particularly at the membrane interface where there is a possibility of hydrosulfurous acid formation.

Two-chambered electrodialytic cells having cation permselective membranes dividing the cell into an anolyte chamber and a catholyte chamber are known in the art. For example, U.S. Pat. No. 2,731,408 and U.S. Pat. No. 2,978,402 disclose such electrodialytic cells. These electrodialytic cells are characterized by the presence of graphite and/or steel electrodes. Silver-lead electrodes are disclosed in U.S. Pat. No. 3,607,694. Lead electrodes are commonly used and prepared in electrolytic lead refining by the Betts process wherein base lead bullion is electrolytically refined to produce a pure lead cathode. The anodes are the cast lead bullion, the electrolyte is a solution of lead fluosilicate and fluosilicic acid. As disclosed in Kirk-Othmer "Encyclopedia of Chemical Technology," vol. 12, 236 (1967) 2d edition, cathode starting sheets are made from pure electrolytic lead, and the lead is deposited upon the cathodes in the electrolytic chamber. The cathode starting sheet made from pure lead and the electrolytically deposited lead are solid, non-porous lead bodies. This type of electrode is a "standard electrode." By use of the term "standard electrode" we mean those electrodes which are found in the prior art and which are made from such materials as steel, zinc, tin, mercury, graphite, non-porous lead, silver-lead alloy, platinum-lead alloy and the like.

Both anolyte and catholyte chambers have been filled with conductive bodies to increase the surface area of the respective anode or cathode and thereby provide low unit area current density. In U.S. Pat. No. 634,271 the anode compartment was filled with broken cast-iron, iron shavings or iron chips. In U.S. Pat. No. 2,815,320, U.S. Pat. No. 2,854,393 and U.S. Pat. No. 2,854,394 porous fillers of a conductive material, such as ion exchange resin beads, are added to chambers of an electrodialytic apparatus. An electrolytic apparatus having a lead shot cathode is disclosed in U.S. Pat. No. 3,457,152. The apparatus is adapted for passage of direct electric current between the anode and the lead shot cathode, and the apparatus has been specifically adapted to the production of adiponitrile from acrylonitrile. Even though the surface area of the electrode is increased by the addition of conductive bodies thereto, the area of the electrodes and in particular the area of the cathode is insufficient to provide a sufficient current density for certain applications where a low unit area current density is required, such as, in the electrodialytic preparation of dithionites from bisulfites. Furthermore, it is generally difficult to fill electrolytic or electrodialytic chambers with the particulate bodies, especially the electrodialytic chambers where sensitive membranes are used and chances of particulate bodies causing rupture, billowing or displacement of the membranes, is increased. Furthermore, in those cases where the electrode itself is formed by the particulate bodies in intimate contact with a standard electrode, the electrode formed thereby is not essentially a single, unit electrode body, but is a conglomeration of small electrode bodies the effectiveness of which depends upon the contact each particle thereof establishes with every other particle and with the standard electrode body. Thus, when particulate bodies are used in chambers as electrodes, they have diminished conductivity of electrical current due to dependence upon contact of particle with particle and particle with standard electrode when compared with the conductivity of a continuous or non-particulate conductive body.

OBJECTS OF THE INVENTION

It is an object of this invention to provide an electrodialytic apparatus and method for the efficient and economical preparation of dithionite.

It is another object of this invention to provide an apparatus and method for the electrodialytic preparation of dithionite from bisulfite in which the dangers of explosion and rapid oxidation of the dithionite are substantially reduced.

It is another object of this invention to provide a lead electrode with substantially increased surface area.

Still another object of this invention is to provide a single, continuous lead electrode capable of substantially filling an electrolytic or electrodialytic chamber.

Another object of this invention is to provide a continuous lead electrode which will permit the circulation of electrolyte within the chamber of an electrolytic or electrodialytic apparatus, said chamber being substantially filled with the lead electrode.

It is a further object of this invention to provide a process for the preparation of a continuous (non-particulate) lead electrode in an electrodialytic or electrolytic apparatus.

Other objects will become evident to those skilled in the art from a reading of this specification and the appended claims and drawings.

SUMMARY OF THE INVENTION

We have found that dithionite may be prepared from bisulfite in an electrodialytic apparatus having at least one anolyte (anode) chamber, at least one catholyte (cathode) chamber adjacent said anolyte chamber, a cation permselective membrane between said anolyte chamber and said catholyte chamber, said catholyte chamber having a spongy, porous, continuous lead cathode substantially defined by the walls of said catholyte chamber and said anolyte chamber having an anode, and a suitable power source. Each chamber has inlet and outlet means and means for circulating a fluid medium therethrough.

A bisulfite-containing solution maintained at less than about 30° C. is circulated through the catholyte chamber of the electrodialytic apparatus, and an acid electrolyte solution is circulated through the anolyte chamber. When an electrical current is imposed across the electrodes, hydrosulfite (dithionite) is cathodically produced from the bisulfite in the bisulfite-containing solution in the catholyte chamber having the continuous, spongy, porous lead electrode.

The continuous, spongy, porous lead electrode is formed as a cathode in an electrodialytic cell having at least one anolyte chamber, at least one catholyte chamber adjacent said anolyte chamber and ion migrating means acting as a barrier to fluid media between said anolyte and catholyte chambers. A plumbite or plumbate salt solution is circulated through the catholyte chamber, and a caustic solution capable of supplying an alkali metal cation to the catholyte chamber is circulated through the anolyte chamber. When an electrical current is imposed across the anode and the standard cathode in the respective chambers, a spongy, porous lead metal is electrolytically deposited at the cathode until the catholyte chamber is substantially filled with a porous, spongy lead metal. Although this deposited electrode is a continuous body with the standard electrode initially placed within the chamber, the deposit is sufficiently porous to permit the passage or circulation of solution through the chamber without interruption of the flow therethrough. By using the term "substantially filled" we mean placing or forming the electrode in the chamber in such a way that the spongy, porous lead electrode occupies either all or nearly all the volume of the chamber.

The continuous, porous lead electrode (cathode) deposited in the catholyte chamber may be left in situ, properly washed, and the apparatus may be used for electrodialytic synthesis, purification and/or separation.

The continuous, porous lead deposit, although somewhat fragile, may be carefully removed from the catholyte chamber of the electrodialytic apparatus and may be used as an electrode in various other chambers as a substitute for a standard electrode or in another electrodialytic apparatus for the preparation of dithionites. A spongy, porous lead electrode is defined herein as the electrode prepared by the electrodialytic process of this invention.

We have also found that the porous lead electrode of the present invention may be regenerated by electrodialytic treatment with caustic solutions when the porous lead electrode becomes fouled and thereby reduces the effective surface area of the electrode which in turn increases the unit area current density.

When dithionite is produced by the electrodialytic apparatus and process of the present invention, and the electrodialytic apparatus and process are integrated with a system of storage reservoirs or chambers, the contents of the reservoir in communication with the catholyte chamber may be protected from atmospheric oxidation effects by establishing a layer of inert liquid hydrocarbon on the surface of the contents of the reservoir vessel.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic representation of a longitudinal cross-section of an electrodialytic cell illustrating pertinent ion formation and transfer for the formation of dithionite ion therein.

FIG. 2 is a diagrammatic representation of a longitudinal cross-section of a two-chambered electrodialytic cell illustrating the formation and transfer of ions pertinent to the formation of the spongy, porous lead cathode.

FIG. 3 is a diagrammatic representation of longitudinal cross-section of a two-chambered electrodialytic cell illustrating the spongy, porous lead cathode formed in the catholyte chamber.

FIG. 4 is a diagrammatic representation of a longitudinal cross-section of a three-chambered electrodialytic cell having two spongy, porous lead cathodes in two catholyte chambers and one anolyte chamber.

FIG. 5 is a diagrammatic representation of a longitudial cross-section of an electrodialytic cell having multiple anolyte and catholyte chambers sharing anode and cathodes respectively.

FIG. 6 is a diagrammatic representation of a longitudinal cross-section of a two-chambered electrodialytic cell in communication with a circulating system including pumps and reservoirs.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As used in FIGS. 1–6 in the accompanying drawings, there is shown a cell frame, 2, preferably of plastic construction, which partially defines the outer portions of the appaartus. Numerals **4** and **6** represent electrodes, the numeral **4** being used to designate the cathode and the numeral **6** being used to designate the anode. In the preferred embodiment of the present invention both the anode and the cathode are prepared from lead sheet material which partially defines the respective chambers in which they are located. Ion migrating means designated by numeral **8**, is an ion exchange membrane of the type which will permit the passage of cations therethrough and is located between cathode **4** and anode **6** in such a way that it separates the cell into chambers designated as catholyte chamber **20** and anolyte chamber **22**. Accordingly, the cell construction of a two-chambered apparatus as shown in FIGS. 1, 2, 3 and 6 comprises a cathode, catholyte chamber, ion migrating means, anolyte chamber and an anode within a suitable cell frame. Provisions must be made in each chamber for the entrance and exit of the circulating electrolyte. In catholyte chamber **20** catholyte enters the chamber at inlet or opening **12** and leaves the chamber at opening or outlet **14**. Anolyte enters the anolyte chamber **22** at inlet **10** and leaves chamber **22** at outlet **16**.

In FIG. 1 hydrosulfite or dithionite formation is shown in ionic form when a bisulfite-containing solution is used as the catholyte, and sulfuric acid is used as the acid anolyte solution. Ionic decomposition of water is also shown in the chambers of the apparatus of FIG. 1.

In FIG. 2 the ionic formation of the spongy, porous lead electrode is shown when plumbite ion-forming solutions are reduced to elemental lead at the cathode. The plumbite-containing solution is circulated in the presence of a caustic solution in the catholyte chamber while a caustic solution such as an aqueous alkali metal hydroxide solution is circulated in the anolyte chamber. Ionic decomposition of water is shown in both chambers of FIG. 2.

In the preferred embodiment of the present invention for making a spongy lead electrode aqueous sodium plumbite is circulated in the anolyte chamber while a dilute aqueous sodium hydroxide solution is circulated in the contiguous anode chamber. When electric current supplied by a suitable power source (not shown), such as a direct current source, is imposed across the electrodes of the electrodialytic apparatus, a mass of spongy, porous lead is deposited at the cathode until the catholyte chamber is substantially filled with the spongy, porous lead. It is important in the practice of the present invention that substantially uninterrupted circulation of the catholyte liquor be carried out while the current is imposed across the electrodes. This electrolytic deposition of spongy, porous lead upon the initial single sheet-like rod, disc or strip electrode greatly increases the cathodic area beyond the planar or cylindrical nature of the original electrode. Due to the nature of the deposition of the lead in the catholyte chamber the deposited lead is also characterized by porosity which permits the flow of catholyte or any electrolyte liquor therethrough and gives the electrode a spongy property.

FIG. 3 illustrates an electrodialytic apparatus having a spongy, porous lead electrode designated by numeral **18** deposited throughout catholyte chamber **20**. The spongy, porous nature of the lead deposited at the cathode and substantially filling the catholyte chamber permits catholyte liquor or any other suitable electrolyte to pass through opening **12** into catholyte chamber **20** and out opening **14**. Lead may be deposited at the cathode in the form of a spongy, porous deposit until the current imposed across the electrodes ceases. By control of current, deposit of spongy, porous lead can be stopped at any time during deposition to provide an electrode body having any amount of spongy, porous lead deposited thereon. Furthermore, by the method of this invention a porous lead electrode having almost any shape or form desired can be produced by varying the shape of the catholyte chamber in the electrodialytic cell. This may be accomplished in view of the fact that the spongy, porous lead electrode is defined by the walls of the catholyte chamber when the electric current is imposed across the electrodes for a sufficient time, and there is sufficient catholyte liquor circulated through the catholyte chamber during the imposition of current.

Once the porous lead electrode is deposited in the catholyte chamber, the plumbite-containing solution can be drained from the catholyte chamber, and the spongy, porous lead electrode can be removed from the chamber. However, it is preferred in the preparation of the dithionites that the porous lead cathode prepared in the catholyte chamber remain in situ and that the catholyte solution as well as the anolyte solution be removed from the respective chambers followed by suitable rinsing of the chambers with water to remove residual electrolytes. When the rinsing is completed, a bisulfite salt containing solution is circulated in the catholyte chamber and an acid electrolyte solution is circulated through the anolyte chamber. Dithionites are formed when an electrical current is imposed across the spongy, porous lead cathode and the anode.

Critical to the economic and efficient formation of the dithionites in the catholyte chamber is the spongy, porous lead electrode which substantially fills the catholyte chamber. The spongy, porous lead cathode permits high planar current density and consequently, short residence time of the circulating liquor.

During the formation of the dithionites in the catholyte chambers, the sponge lead electrode may accumulate lead sulfide formed as a side reaction, and thereby decrease the activity of the dithionate formation within the chamber. We have found that circulation of a sodium hydroxide solution through the catholyte compartment under an imposed potential will remove the lead sulfide and restore full activity in situ, without necessity of cell disassembly. About a 2 N aqueous solution of sodium hydroxide is suitable for removing the lead sulfide accumulation. This regeneration of the sponge lead electrode is represented by the reaction of sodium hydroxide and lead sulfide to form sodium plumbite which under the imposed potential re-deposits the lead at the cathode. Any suitable caustic solution which forms a soluble plumbite salt, in the presence of lead sulfide, may be used as cathode regenerant. One skilled in the art can select a suitable concentration range for the caustic solution.

In the preferred embodiment of the present invention sodium bisulfite is circulated in an aqueous solution at less than about 30° C. in the catholyte chamber of the electrodialytic apparatus containing the spongy, porous lead cathode. The sodium bisulfite may be made available by either dissolution of sodium metabisulfite in water in accordance with the following equation:

$$Na_2S_2O_5+H_2O\rightarrow 2NaHCO_3$$

or by the passage of sulfur dioxide into sodium hydroxide or sodium carbonate. Although sodium bisulfite or sodium metabisulfite are the preferred bisulfite salts for the formation of dithionite salts of the present invention, other bisulfite salts, such as, the potassium salt, the magnesium salt, the zinc salt, and the like or mixtures thereof may be converted to their corresponding hydrosulfites or dithionites. The bisulfite salt of the present invention must be water-soluble or partially soluble in water and when used as catholyte, it is used as an aqueous solution. As used herein, a bisulfite salt-containing solution is any bisulfite salt or bisulfite salt precursor capable of forming a bisulfite salt, dissolved completely or partially in water. Although the pH of the circulating bisulfite salt-containing solution may be of from about 2.5 to 6.0, it is preferred that the pH be from about 3.0 to about 4.5 for the cathodic reduction of the bisulfite ion to the hydrosulfite ion.

The hydrosulfite or dithionite is totally unstable at a pH below about 2.0 having a half-life depending upon the degree of acidity, measurable in minutes or seconds. The hydrosulfite exhibits maximal stability at a pH range of from about 7 to 10, but at a pH of about 7 to 10 the catholyte solution is essentially a solution of sodium sulfite which is cathodically reduceable, but yields substantial quantities of sodium sulfide. Accordingly, to prevent high yields of sodium sulfide the pH of the circulating catholyte solution should be less than about 7.0.

The anolyte liquor used in the preparation of the dithionites is preferably a dilute sulfuric acid solution containing about 5% (by weight) sulfuric acid in water. However, suitable concentrations of sulfuric acid which may be used as the anolyte liquor may be selected by one skilled in the art. When sulfuric acid is used as the anolyte, the sulfuric acid breaks down into hydrogen ion, bisulfate ion and sulfate ion. The hydrogen ion migrates from the anolyte chamber into the catholyte chamber through the cation permselective membrane disposed between the two chambers. Although aqueous sulfuric acid solution is the preferred anolyte liquor in the preparation of the dithionites, other aqueous acid electrolyte solutions, such as phosphoric acid, may be used in lieu thereof. One skilled in the art can select a suitable acid electrolyte solution and concentration for circulation as anolyte liquor.

In the preparation of the dithionites it is preferred that the temperature of the catholyte liquor be maintained at temperatures of about 20–25° C. and at no time in excess of 30° C. Although temperatures lower than 20° C. may be used, it is preferred that the lowest operating temperature be about 20° C. At temperatures in excess of 25° C., and particularly in excess of 30° C., extreme precaution must be exercised because of the thermal instability of the dithionites, particularly at the membrane interface where hydrogen ion enters the catholyte liquor and forms hydrosulfurous acid. At temperatures of 25° C. or less the possibility of thermal instability is substantially decreased.

Any hydrosulfite or dithionite salt formed by the cathodic reduction of the aqueous bisulfite salt-containing solution is designated herein as hydrosulfite, hydrosulfite salt or aqueous hydrosulfite salt solution.

In the formation of the spongy lead electrode, it is preferred that sodium plumbite be circulated as the catholyte liquor in the presence of an aqueous solution of sodium hydroxide or other suitable alkali metal, alkaline earth metal hydroxide or caustic solution and the like. Sodium plumbite,, Na_2PbO_2 or $Na_2[Pb(OH)_4]$, can be formed or prepared from lead monoxide and sodium hydroxide. However, any of the other corresponding alkali metal hydroxides or alkaline earth metal hydroxides and the like may be used with lead monoxide (litharge), PbO, to form the corresponding water-soluble plumbite salt. Any water-soluble plumbite salt, plumbate salt, or a suitable source therefor and mixtures thereof may be used in the formation of the sponge lead electrode of the present invention and as used herein a plumbite salt, alkali metal plumbite salt, alkaline earth metal plumbite salt or any other plumbite salt source is designated as a plumbite salt. Alkali metal plumbate salt, alkaline earth metal plumbate, plumbate salt or any other plumbate salt source is referred to herein as plumbate salt. Critical to the process of the present invention is the water solubility or partial water solubility of the plumbite or plumbate salt.

The anolyte solution used in the apparatus during the preparation of the spongy, porous lead electrode is preferably an alkali metal hydroxide, or carbonate, such as, sodium hydroxide, sodium carbonate or potassium hydroxide, and the like, or mixtures thereof. As used herein caustic solution refers to any suitable alkali or alkaline earth metal hydroxide or carbonate and the like, including mixtures thereof normally used in electrodialysis as electrolyte solutions. A dilute aqueous solution of the caustic material may be used in the anolyte solution, it being preferred that about 2 N sodium hydroxide solution (in water) be used as the anolyte liquor, when sodium hydroxide is used as the anolyte liquor. However, a concentration of the caustic solution or alkali metal hydroxide suitable for use in the anolyte liquor may range from about 0.5 N to 3.0 N, it being within the purview of one skilled in the art to select the proper caustic solution at the proper concentration.

The ion migrating means which separates anolyte and catholyte chambers used in the preparation of the dithionites can be any material which selectively permits the passage of cations in the direction of the cathode and rejects the passage of anions in the direction of the anode. This role is filled by cation exchange membranes. Cation exchange (cation permselective) membranes are also preferred and recommended as the ion migrating means in the production of the spongy, porous lead electrodes. Cation permselective membranes minimize excessive diffusion of the oxidation sensitive dithionite (hydrosulfite) and bisulfite anions and yet permit hydrogen ion or other cation to reach the catholyte chamber. Recommended cation exchange membranes are those polystyrene-based sulfonated cation exchange membranes manufactured by Ionac Chemical Company as NC–3142 and NC–3470. The ion migrating means used to separate the anode and cathode chambers of the electrodialytic apparatus used to prepare the spongy lead electrode may be cation permselective or non-selective (neutral). Thus, to prepare the spongy, porous lead electrode the ion migrating means can be any material which selectively permits the passage of cations in the direction of the cathode and may be designated as cation migrating means. A neutral membrane is a membrane which permits the migration of anions and cations. When the neutral membrane is the ion migrating means between anode and cathode chambers in the electrodialytic apparatus used to prepare the spongy, porous lead electrode, there is some loss of plumbite or plumbate to the anode. However, because of the predominance of hydroxyl ion and its superior mobility in the catholyte solution, there is a preferential transport of the hydroxyl ion and an opportunity for a significant amount of reduction of the plumbite or plumbate ion to elementary lead.

The standard electrodes provided in the electrodialytic apparatus of the present invention may be any suitable conductive material and may be selected by one skilled in the art. Examples of electrode material are graphite, several lead alloys including a silver-lead and a platnium-lead alloy, lead, steel, zinc and the like. The cathode upon which the spongy, porous lead electrode is deposited from the plumbite-containing solution can be any conductive material which will form an intimate contact with the spongy, porous lead which deposits thereon. Although the electrodes may assume several varying shapes such as sheets, strips or cylinders it is preferred in the practice of the present invention that the electrodes assume the shape of rectangular sheets and thereby define one wall of the chamber in which it is located. Cell construction may be varied such that a single electrode series as the electrode for two contiguous or adjacent chambers having electrodes of the opposite charge, such as, the single anode source shown in the three-chambered cell of FIG. 4.

Another embodiment of the present invention is represented in FIG. 4 where a three-chambered apparatus having two catholyte chambers designated by numeral **20** which are filled with a porous lead cathode designated by numeral **18** previously deposited upon cathodes designated by numeral 4 and one anolyte chamber designated by the numeral **22** having an anode designated by number **6**, is shown. The two catholyte chambers are separated from the centrally located single anolyte chamber by two ion migrating means designated by numeral **8** which are preferably a cation permselective membrane, and a single anode serves as the anode source for two cathodes. In the operation of the apparatus of FIG. 4 anolyte is circulated in anolyte chamber **22** while catholyte is circulated in catholyte chambers **20**. When the electrical current is imposed across the electrodes cathodic reduction of the bisulfite takes place in the two catholyte chambers. When the spongy, porous lead cathodes are formed in the three chambered apparatus of FIG. 4, anolyte chamber **22** is common to both of the adjacent catholyte chambers designated by numeral **20**, and when an electrical current is imposed across the electrodes the spongy, porous lead deposits upon the cathodes by cathodic reduction of the plumbite salts, in both chambers simultaneously.

FIG. 5 represents still another embodiment of the present invention showing a stack of two-chambered electrodialytic cells in which, except for the end chambers, a single electrode is common to two chambers. In an apparatus, such as the one designated in FIG. 5, there is a maximum utilization of the electrode surfaces of all electrodes except those positioned at both ends of the cell where only one surface of the electrode is used, and as shown in FIG. 5, cathode **4** is the electrode positioned at each end of the stack. The two-chambered cells as illustrated in FIG. 5 may be stacked to include up to 30 or more chambers having the configuration of cathode, catholyte chamber, cation permselective membrane, anolyte chamber, anode, anolyte chamber, cation permselective membrane, catholyte chamber, cathode, catholyte chamber, cation permselective membrane, anolyte chamber, etc. Although FIG. 5 illustrates a stack of two-chambered electrodialytic cells starting with the cathode and catholyte chamber, it is within the purview of one skilled in the art to produce a stack of two-chambered cells wherein the first members of the stack are an anode and anolyte chamber. In the embodiment illustrated in FIG. 5, a single anode is common to two anolyte chambers and a single cathode source serves two catholyte chambers having spongy, porous lead electrodes. A cathode source is used herein to define the "standard" cathode upon which the spongy, porous lead metal is deposited.

In FIG. 6 we have shown a complete circulating system feeding a two-chambered electrodialytic apparatus, the numerals of which designate the same elements of the cells in FIGS. 1–5 above. In the system as shown in FIG. 6, two reservoirs are provided one for the anolyte chamber designated as reservoir **30**, and one for the supply of the catholyte chamber designated as reservoir **40**. Reservoir **30** contains water and sulfuric acid during the cathodic reduction of the bisulfite containing solution and reservoir **30** contains water, the bisulfite containing solution such as sodium bisulfite, and the dithionite produced as a result of the cathodic reduction of bisulfite and shown in reservoir **40** as sodium dithionite. A pump designated by numeral **42** removes the aqueous solution from reservoir **40** by a conduit **41** and forces the solution removed from reservoir **40** into catholyte chamber **20** at inlet **12** through conduit **44**. This catholyte solution or liquor comprising water and sodium bisulfite initially, and, after cathodic reduction, water, sodium bisulfite and sodium dithionite, passes through the catholyte chamber containing the sponge lead cathode where it is subjected to cathodic reduction. The electrolyte liquor from reservoir **40** then passes from catholyte chamber **20** through catholyte chamber outlet **14** into conduit **46** where it returns to reservoir **40** for recirculation and further cathodic reduction.

A layer designated by numeral **48**, is shown covering the catholyte liquor of reservoir **40**. Layer **48** represents a hydrocarbon or other inert material which will not react with the catholyte liquor but which will prevent air from entering or contacting the catholyte liquor. Kerosene is one of the preferred hydrocarbons which may be used in layer **48**. Other hydrocarbons which may be used in the layer are mineral oil, number 2 fuel oil, and the like. One skilled in the art can select a suitable hydrocarbon to prevent exposure of the liquor to air. Catholyte liquor passing from catholyte chamber **20** through conduit **46** into reservoir **40** is preferably admitted to reservoir **40** beneath layer **48** so that the catholyte liquor is not exposed to air. It is also deemed within the purview of one skilled in the art to use an inert atmosphere above the catholyte liquor to prevent exposure of the liquor to air.

The anolyte liquor comprising water and an acid solution, such as sulfuric acid, is removed by pump **32** from reservoir **30** by conduit **31** and passes by means of conduit **34** into opening **10** of anolyte chamber **22**. The anolyte liquor passes from anolyte chamber **22** through opening **16** and is recirculated back into reservoir **30** by means of conduit **36**. Any circulating means may be used to cause a flow of electrolyte solutions through the respective chambers, and for continuous operation of the apparatus of this invention it is preferred that a mechanical pump be used for such circulating means. It is within the purview of one skilled in the art to select suitable means for circulating the electrolyte solutions.

Although the drawing in FIG. 6 shows a catholyte liquor comprising bisulfite and dithionite and an anolyte liquor comprising water and sulfuric acid, in the preparation of the sponge lead electrode, reservoir **30** or an alternative reservoir may be filled with a caustic solution, such as sodium hydroxide, and reservoir **40** or an alternative reservior may be filled with a plumbite salt solution and an alkali metal hydroxide or carbonate solution, alkaline earth metal hydroxide or carbonate solution, or other caustic solution.

When multiple catholyte chambers are provided, such as in FIGS. 4 and 5, the catholyte liquors can be circulated to and from a single reservoir or each catholyte chamber can utilize its own reservoir and pumping system. Furthermore, when there is more than one catholyte chamber the effluent from one catholyte chamber can be circulated to one of the other catholyte chambers and used as the influent in that particular catholyte chamber. The effluent from the second catholyte chamber can be used as the influent of a third catholyte chamber, etc. until the desired cathodic reduction of bisulfite has been attained in the catholyte liquor, or in the alternative, the catholyte liquors can be returned at any point in the system to the catholyte reservoir where it will be recirculated. Anolyte liquors may be circulated from chamber to chamber as described above for the catholyte liquor, or the anolyte liquor can be returned to the reservoir and recirculated. It is within the purview of one skilled in the art to replenish the anolyte liquor with acid when the acid concentration of the anolyte liquor becomes diminished to the point where it is no longer effective as an anolyte (electrolyte).

In the operation of the apparatus the concentration of the dithionite in the catholyte liquor increases as the concentration of the bisulfite decreases. Recirculation of the catholyte liquor is generally terminated when the dithionite concentration reaches the desired level. This generally may be determined by the darkening of a lead acetate test solution which is an indicator for sulfite ion. At the terminal period of the bisulfite reduction there is an increase in pH as the product, sodium dithionite (hydrolytically), alkaline in pure solution due to the weak acid hydrosulfurous acid, and the strong base, NaOH, forms. As the concentration of sodium dithionite becomes excessive, and the pH of the catholyte liquor increases, sodium sulfite forms and is cathodically reducible to sodium sulfide. The sodium sulfide causes the darkening of the lead acetate test solution. Thus, when the lead acetate test solution begins to darken, the terminal point of the cathodic reduction of the bisulfite has been reached. This is generally defined as the desired level of dithionite salt.

Although an upward flow has been shown by the arrows in FIGS. 1–6, the invention is not limited to the direction of the flow of the anolyte and catholyte liquors, and accordingly, there may be a downward flow of the liquors or there may be a combination of upward and downward flow of the liquors (in separate chambers).

In order to maintain the temperatures of the electrodialytic system at less than 30° C. and preferably no higher than about 20–25° C., it is necessary either to provide for cooling of the electrodialytic apparatus or the cooling of the electrolyte solutions or both. Sufficient heat transfer may be possible by circulating cooling water directly past one of the electrodes through an adjoining chamber or by cooling the contents of the reservoir vessels from which catholyte and anolyte are drawn and returned by cooling means such as for example a refrigerating unit or cooling water coils.

The power source for the apparatus of the present invention may be any suitable rectifier capable of delivering sufficient direct current for the cathodic reduction of the plumbite or plumbate salts and the bisulfite or metabisulfite salts, and can be selected by one skilled in the art.

Although it is not necessary to the practice of the present invention, it is preferred to pretreat the anode to build an adherent lead oxide, PbO_2, coating on the anode. This is preferably done by imposing an electrical potential across the electrodes when the anolyte is an acid solution, prefearbly a 10% (by weight) sulfuric acid solution, and the catholyte is a salt of a sulfate, such as sodium sulfate, or similar salt in a concentration of about 15% by weight in an aqueous solution. These electrolyte liquors are circulated for approximately 24 hours under an imposed potential to coat the anode properly. Suitable anolyte acids, catholyte salt solutions and concentrations thereof for this purpose can be determined by those skilled in the art.

The process of the present invention can be carried out in the presense of electrolyte impurities and adjuvants which do not adversely effect the cathodic reduction of the bisulfite or metabisulfite in the preparation of the dithionite.

Valves, vents, gauges, meters, conduits and the like can be used in the process and apparatus of the present invention, and it is within the purview of one skilled in the art to utilize such equipment and devices.

EXAMPLES

Description of a two-chambered cell

Two rigid polyvinyl chloride (PVC) cell frames, outer dimension 8" (inches) by 8", inner dimensions 5⅜" by 5⅜", affording an active area of 27½ square inches relative to a membrane mounted between them or the electrodes at either end were used in the construction of an electrodialytic apparatus. Lead sheets having dimensions of 8 inches by 10 inches were used as cathode and anode. A sulfonated, polystyrene cation exchange membrane manufactured by Ionac Chemical Company and designated as Ionac MC 3470 was mounted between neoprene gaskets and sandwiched in turn between a pair of gasketed, perforated, rigid PVC anti-billow sheets which were ⅛ inch thick. Electric connections were made to the lead sheets by 1/16 inch thick by ½ inch wide copper strips to a rectifier capable of furnishing a maximum of 10 amperes at a maximum of 20 volts. The cell was terminated at each end by ½ inch thick rigid PVC 8 inch by 8 inch end plates, and the entire assemblage comprising end plate, anode, anti-billow sheet, membrane, anti-billow sheet, cathode, and end plate with included gaskets, was compressed by suitably spaced C clamps. The cell frames were also included in the assemblage of the other elements. Each of the cell frames was tubulated at the center of the base and the top with rigid PVC nipples of 3/16 inch inner diameter, and plastic tubing was attached to these nipples to provide upflow circulation of anolyte and catholyte by means of two pumps connected to aspirator bottles. The anolyte reservoir was a single-necked aspirator bottle of one-liter capacity. The catholyte reservoir was a three-necked aspirator bottle of 2-liter capacity. Both anolyte and catholyte reservoirs were mounted inside stainless steel trays of 4 inch depth and equipped with spouts at their base, and a rapid stream of cold tap water was circulated in the trays. This permitted maintenance of a temperature in the anolyte and catholyte reservoirs of 20° to 25° C.

Preparation of anode

Ten perecnt (by weight) H_2SO_4 as anolyte and 15% (by weight) sodium sulfate as catholyte were circulated for 24 hours at 3 amperes to build an adherent lead oxide, PbO_2, coating on the anode.

Preparation of cathode

Lead monoxide, PbO, 46.0 grams, dissolved in 134 ml. of 50% boiling NaOH (in water) was diluted to 750 ml. with water and introduced into the catholyte reservoir of the above described apparatus. One liter of aqueous 2 N NaOH was introduced into the anolyte reservoir. After the pumps were actuated and the two-cell chambers were filled with the respective liquors, the rectifier was set to furnish 4 amps at 2.0 volts for 7 minutes, then raised to 80 amps at 2.8 volts and held at the latter amperage for 3 hours. The entire system was drained and the cathode portion was flushed repeatedly with demineralized water until a mildly alkaline pH (pH of about 7.0 to about 10) characterized the wash water. The system was again completely drained.

EXAMPLE 1

Preparation of dithionite

An anolyte solution or liquor comprising 700 ml. of 5% (by volume) sulfuric acid in water was placed in the anolyte reservoir. A catholyte liquor comprising 600 ml. of 20% (by weight) sodium metabisulfite, $Na_2S_2O_5$ (anhydride form of sodium bisulfite, $NaHSO_3$), in water and 350 ml. of deodorized, colorless kerosene were placed in the catholyte reservoir. The kerosene formed a layer on the top of the sodium metabisulfite solution and protected both the bisulfite and the ultimately formed hydrosulfite or dithionite from atmospheric oxidation. Tubing leading into the reservoir from the catholyte chamber was adjusted so that it extended beneath the kerosene layer. Table I below shows the time of operation of the cell, amperage, voltage and percentage of sodium dithionate obtained in Example 1.

TABLE I

Time, hours	Amperage	Voltage	Percent sodium dithionite
1	10	4	4.05
1.5	10	4	5.28
2.0	10	4	5.80

An examination of Table I indicates that after one hour of operation at 10 amps and 4 volts, a concentration 4.05% (by weight) of sodium dithionite was prepared from the sodium metabisulfite. After 2.0 hours of operation, 5.8% sodium dithionite (sodium hydrosulfite) had been formed in the catholyte solution.

The amount of sodium dithionite was determined by an Indigo Carmine test adapted with some minor modifications from the method disclosed in Scott's "Standard Methods of Chemical Analysis" (5th edition), vol. I, page 930. The Indigo Carmine (3.732 grams) is dissolved in strong sulfuric acid solution (75 ml. $H_2SO_4/1500\ H_2O$) and diluted with water to a volume of 2.0 liters. Twenty-five milliliters of this solution is placed in a flask. Sodium bicarbonate (about 4 to 5 grams) is placed in a convenient vessel for immediate use. The sodium bicarbonate is quickly added to the 25.0 ml. of indigo carmine solution and the catholyte liquor or solution containing the hydrosulfite is then added to the sodium bicarbonate-containing solution dropwise, from a pipet, when the CO_2 effervescence has mainly but not completely subsided, until the original intense blue color has been bleached to a light yellowish-green. If the titration has been properly run (time-wise) there remains sufficient CO_2 to hold or maintain the color for a few seconds. Since 25.00 ml. of Indigo is equal to 0.0174 gram of sodium dithionite, the percent of sodium dithionite may be calculated in accordance with the following equation:

$$\frac{0.0174\times100}{\text{Ml. of } Na_2SO_4}\text{ solution}=\text{Percent } Na_2S_2O_4$$

EXAMPLE 2

Using the cell described above, an anolyte liquor containing 30 ml. concentrated H_2SO_4 in 970 ml. water and a catholyte liquor of 750 ml. of 20% (by weight) $Na_2S_2O_5$, the results shown in Table II were obtained.

TABLE II

Time, hours	Amperage	Voltage	Temperature, ° C.
0	10	4	26
0.5	10	4.8	26
1.1	10	4.5	26
1.75	10	4.5	26

After one hour and forty-five minutes of operation in accordance with Table II, 0.32 ml. catholyte liquor was required to convert the blue color of the indigo solution to the desired yellowish-green color. Thus, 5.44% of the catholyte liquor was sodium dithionite after 1.75 hours of operation under the designated conditions.

EXAMPLE 3

Using the electrodialytic apparatus disclosed above, anolyte liquor of 30 ml. concentrated sulfuric acid in 970 ml. of water and a catholyte liquor of 850 ml. of a 20% (by weight) sodium metabisulfite under the conditions set forth in Table III below, after 2.35 hours of operation it was determined that the catholyte liquor contained 6.74% sodium dithionite.

TABLE III

Time, hours	Amperage	Voltage	Temperature, ° F.
0	10	4.8	25
2.35 [a]	10	4.2	27

[a] Final titre: 0.26 ml. catholyte/25.00 ml. Indigo. Current efficiency calculated at 75.5%.

EXAMPLE 4

A two-chambered electrodialytic apparatus was assembled as described above. Instead of depositing a spongy, porous lead electrode as described above, fine lead shot in the form of spheres was added to the catholyte chamber until the catholyte chamber was filled with the spheres. Circulation of the liquors disclosed in Example 1 produced negligible quantities of the sodium dithionite.

EXAMPLE 5

A two-chambered electrodialytic apparatus was assembled in accordance with the description given above. The anode was prepared in accordance with the process described above, and the spongy, porous, lead cathode was made in accordance with the process of this invention. After the system was drained, the cell was disassembled carefully and the spongy, lead cathode was removed from the chamber. The electrode was soft and spongy to the touch and appeared to have a fine porosity capable of permitting the passage of fluid therethrough. The spongy, porous lead electrode was defined by the space of the chamber walls and adhered to the original lead electrode sheet which had been inserted in the catholyte chamber.

In accordance with the objects of the present invention an electrodialytic apparatus and process have been defined for the preparation of dithionites from bisulfites. Also, in accordance with the objects of the present invention a spongy, porous lead electrode has been prepared in an electrodialytic apparatus by an electrodialytic process, and said spongy, porous lead electrode has been utilized in the electrodialytic preparation of dithionites from bisulfites.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

We claim:

1. A process for the electrodialytic formation of a hydrosulfite salt comprising:

(a) providing an electrolytic cell having an anolyte chamber, at least one catholyte chamber adjacent said anolyte chamber, a cation permselective membrane between said chambers, said catholyte chamber having a spongy, porous lead cathode substantially defined by the walls of said chamber, said cathode being of the type prepared by the cathodic reduction of plumbite or plumbate salt sources in the catholyte chamber of an electrodialytic apparatus while catholyte comprising plumbite or plumbate salt sources is circulated through the chamber, and said anolyte chamber having an anode, inlet and outlet means in each chamber and means for imposing an electrical current across said cathode and said anode;

(b) circulating an aqueous bisulfite salt-containing catholyte solution through said catholyte chamber;

(c) circulating an aqueous acid electrolyte solution through the anolyte chamber; and

(d) imposing an electrical current across the anode and cathode whereby a hydrosulfite salt is produced from the bisulfite salt in the catholyte chamber having the spongy, porous lead electrode.

2. A process in accordance with claim **1** wherein the bisulfite salt-containing solution circulating through the catholyte chamber has a concentration in excess of about 20% (by weight) bisulfite salt.

3. A process in accordance with claim **1** wherein the bisulfite salt-containing solution is sodium bisulfite.

4. A process in accordance with claim **1** wherein the bisulfite salt-containing solution is sodium metabisulfite.

5. A process in accordance with claim **1** wherein the aqueous acid electrolyte solution circulating through the anolyte chamber is a dilute sulfuric acid solution.

6. A process for the electrolytic formation of sodium hydrosulfite comprising:

(a) providing an electrolytic cell having an anolyte chamber, at least one catholyte chamber adjacent said anolyte chamber, a cation permselective membrane between the anolyte and catholyte chambers, said catholyte chamber having a cathode and said anolyte chamber having an anode, inlet and outlet means in each chamber and means for applying a difference in potential to the anode and cathode;

(b) circulating an aqueous solution of sodium plumbite through the catholyte chamber;

(c) circulating an aqueous solution of sodium hydroxide through the anolyte chamber;

(d) imposing an electrical current between the anode and the cathode to deposit lead metal from the sodium plumbite at the cathode until the catholyte chamber is filled with a spongy, porous lead material;

(e) draining the liquors from the anolyte and catholyte chambers and rinsing said chambers;

(f) circulating an aqueous catholyte solution selected from the group consisting of sodium bisulfite and sodium metabisulfite and mixtures thereof having a concentration in excess of about 20% by weight and a pH of about 2.5 to 6.0 through the catholyte chamber;

(g) circulating a dilute aqueous sulfuric acid solution through the anolyte chamber; and

(h) imposing an electrical current across the electrodes while maintaining the temperature of the aqueous catholyte solution selected from the group consisting of sodium bisulfite and sodium metabisulfite and mixtures thereof at less than about 30° C.,

whereby sodium hydrosulfite is produced from the sodium bisulfite in the catholyte chamber having the spongy, porous lead electrode.

7. A process for the electrolytic formation of sodium hydrosulfite comprising:

(a) providing an electrodialytic cell having an anolyte chamber, at least one catholyte chamber adjacent said anolyte chamber, a cation permselective membrane between the anolyte and catholyte chambers, said catholyte chamber having a spongy, porous lead cathode substantially filling said chamber, said cathode being of the type prepared by the cathodic reduction of plumbite or plumbate salts in the catholyte chamber of an electrodialytic apparatus while catholyte comprising plumbite or plumbate salt source is circulated through the chamber, and said anolyte chamber having an anode, inlet and outlet means in each chamber and means for applying an electrical potential across said anode and cathode, said catholyte chamber communicating with a reservoir by suitable conduits and circulating means and said anolyte chamber communicating with a reservoir by suitable conduits and circulating means;

(b) providing an aqueous bisulfite salt-containing solution in said catholyte chamber and its respective reservoir;

(c) circulating an aqueous acid electrolyte solution through the anolyte chamber and its respective reservoir by said circulating means;

(d) providing an inert, non-reactive protective layer on the surface of the aqueous bisulfite salt-containing solution in the reservoir communicating with said catholyte chamber;

(e) circulating said aqueous bisulfite salt-containing solution by said circulating means from said catholyte chamber to its respective reservoir by a conduit extending below the surface of said inert, non-reactive, protective layer; and

(f) imposing an electrical current across the electrodes whereby a hydrosulfite salt is produced from the bisulfite salt in the catholyte chamber having the spongy, porous lead electrode, and hydrosulfite salt formed thereby is stored beneath said inert, non-reactive protective layer which excludes atmospheric air from said hydrosulfite salt.

8. A process in accordance with claim 7 wherein said inert, non-reactive, protective layer is a hydrocarbon.

9. A process in accordance with claim 8 wherein said hydrocarbon is kerosene.

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FREDERICK C. EDMUNDSON, Primary Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,748,238 Dated July 24, 1973

Inventor(s) Allyn H. Heit and James N. Williamson

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

Column 12, line 27, "80 amps" should be -- 8.0 amps --.

Signed and sealed this 15th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

PO-1050
(5/[illegible])

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,748,238 Dated July 24, 1973

Inventor(s) A. H. Heit 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 6, line 63, "$2NaHCO_3$" should be -- $2NaHSO_3$ --.

Column 7, line 13, "reduceable" should be -- reducable --.

Column 8, line 75, "number 6" should be -- numeral 6 --.

Column 13, line 9, "gram" should be -- grams --.

Column 13, line 46, "Temperature, °F" should be -- Temperature, °C. --.

Signed and sealed this 8th day of January 1974.

(SEAL)
Attest:

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