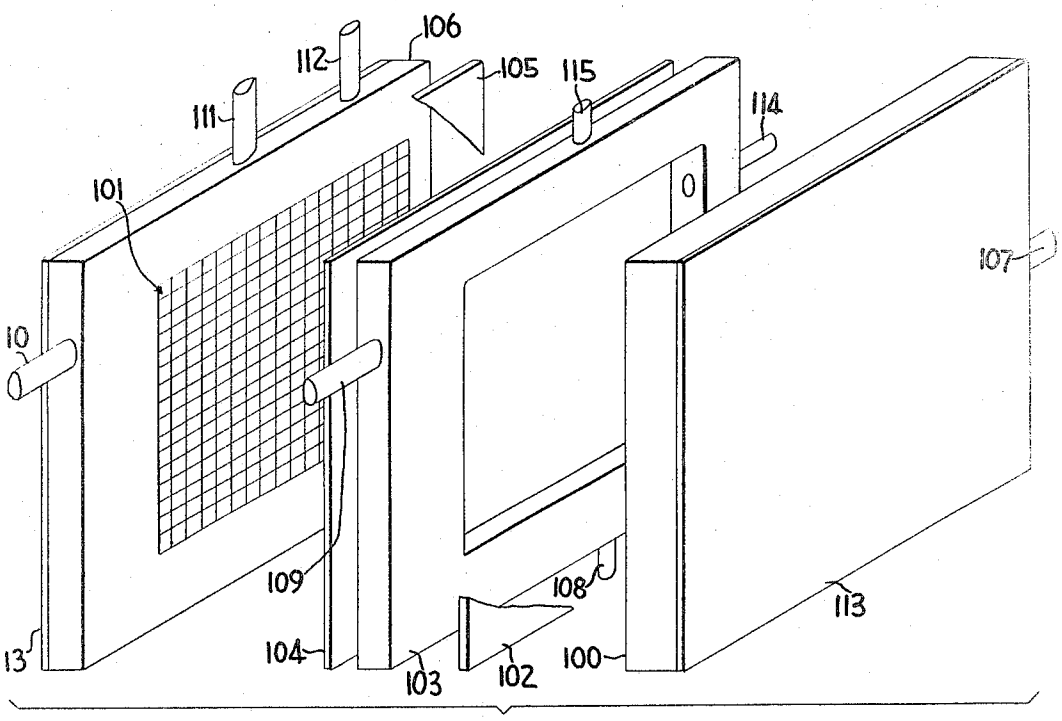
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ELECTROLYTIC PRODUCTION OF DICHROMATES

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ELECTROLYTIC PRODUCTION OF DICHROMATES

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This invention relates to a method of producing sodium dichromate. More particularly, this invention relates to the electrolytic process for the production of sodium dichromate employing an electrolytic cell containing therein a permionic barrier.

Herein described is a novel process for producing sodium dichromate in a permionic compartmental electrolytic cell. In this type of cell, the anode and cathode are separated by a permionic barrier, thus forming an anode compartment and a cathode compartment. These barriers comprise either a membrane or coated diaphragms. Such membranes and coated diaphragms comprise synthetic polymeric or natural or synthetic inorganic materials which are capable of transmitting or passing alkali metal ions therethrough but are incapable of transmitting or passing substantial amounts of chromate ion. In addition, these types of barriers are unique insofar as they prevent the passage of large amounts of product surrounding the anode into the cathode compartment of the electrolytic cell. Thus, the product (catholyte) recovered in the cathode compartment is substantially free of the product (anolyte) present in the anode compartment of the cell. An example of such a cell can be found in copending United States application, Serial No. 29,559, filed May 17, 1960, and now Patent No. 3,236,898.

Sodium dichromate of high purity and high yields may be readily produced by introducing sodium chromate to the anode compartment of the aforementioned permionic compartmental electrolytic cell and withdrawing the liquor contained within the anode compartment when it acquires a pH of 1.5 to 5, preferably between a pH of 2.5 to 5, and most desirably between a pH of 2.5 to 3.5.

Sodium chromate may be added to the anode compartment of the cell as a solid, as part of an aqueous slurry, and most preferably, as an aqueous solution. If solid sodium chromate is added to the anode compartment, it is important that water be also provided therein. When the sodium chromate is added to the anode compartment as an aqueous solution, the CrO_3 content should be from 50 to 550 grams per liter, preferably from 290 to 350 grams per liter.

In a preferred operation of the process of this invention, an aqueous solution containing sodium chromate as obtained from the alkali roasting of chrome ore, such as chromite, is fed to the anode compartment. The roasting process comprises contacting the chrome ore with alkali metal hydroxide or alkali metal carbonate, preferably sodium hydroxide or sodium carbonate, and heating to a temperature between 900 to 1200° C. The alkali treated chrome ore is then leached with water in an amount sufficient to produce an alkaline aqueous solution containing from about 5 to 57 percent by weight of sodium chromate, typically from 20 to 55 percent by weight of sodium chromate, and under preferred operation from 30 to 50 percent by weight of sodium chromate.

The resulting alkaline solution is then added to the

anode compartment of a permionic compartmental electrolytic cell and on electrolysis the pH of the liquor contained within the anode compartment is progressively reduced. When the pH falls within the range described above, the liquor contained within the anode compartment is removed, giving an aqueous solution containing substantially pure sodium dichromate, typically of a purity in excess of 99 percent by weight thereof, and in most cases 100 percent purity, basis weight of sodium dichromate. In addition, this process provides sodium dichromate yields typically in excess of 99 percent of that theoretically obtainable and in most instances provides 100 percent yields.

The concentration of sodium dichromate in the anode liquor is dependent upon the amount of sodium chromate added to the anode compartment. For example, if one desires to produce a saturated aqueous sodium dichromate solution, then solid sodium chromate may be fed to the anode compartment simultaneous with the addition of aqueous sodium chromate solution. The solid Na_2CrO_4 is added in amounts such that on extended residence time of the liquor in the anode compartment, a saturated sodium dichromate solution is produced. On the other hand, a dilute sodium dichromate solution may be produced by adding a more dilute aqueous solution of sodium chromate to the anode compartment.

The liquor (anolyte) formed in the anode compartment, on removal therefrom, may be commercially utilized as obtained. Sodium dichromate liquor obtained from the aforementioned process may be processed according to conventional techniques to isolate the dihydrate or the anhydrous variety from solution. Solid anhydrous sodium dichromate or a more concentrated solution may be obtained by evaporating the solution, typically at a temperature of from 100 to 127° C. Usually, a 70 percent by weight aqueous sodium dichromate dihydrate solution is the preferred solution form for commercial utilization.

The product produced in the cathode compartment of the permionic cell may be sodium hydroxide, sodium carbonate, or a mixture of sodium hydroxide and sodium carbonate. Sodium hydroxide is produced in the catholyte when water free of substantial amounts of other anions is added to the cathode compartment. On the other hand, when CO_2 is added to the water, sodium carbonate is obtainable. In a desirable embodiment of this process, sodium carbonate is introduced to the catholyte to form an aqueous solution comprising a mixture of sodium hydroxide in sodium carbonate. This product may be removed from the cell and carbonated to produce sodium carbonate, sodium sesquicarbonate or sodium bicarbonate as hereinafter described.

The electrolytic cell, as described above, comprises an anode and a cathode separated by a barrier positioned intermediate in the cell or close to either one of the electrodes. Preferably, the barrier contacts the cathode and the anode is spaced a small distance from the barrier. The closer the anode is to the cathode, the lower is the resistance in the cell and hence, the lower is the voltage requirement necessary to achieve electrolysis. The barrier, as a rule, is a blade or a sheet which is capable of being supported in the cell and effecting the proper separation of the solutions contained about said anode and said cathode.

The barrier may be termed a membrane or a solid material over which is coated the proper permionic material. Illustrative of such membranes are organic plastic materials coated on substrates or self-supporting films of organic plastic materials, such as asbestos diaphragms impregnated with organic polymeric materials.

Examples of materials which serve to allow transmission (passage) of sodium ion through the barrier but prevent the transmission of chromate ions and chromic acid include cross-linked organic polymers containing thereon carboxylic acid or carboxylic acid forming radicals. Instead of carboxylic acid, there may be substituted therefor inorganic acid type radicals such as sulfonyl radicals, sulfate radicals, phosphoro radicals, phosphonyl radicals and nitrosyl radicals. Illustrative of known polymeric materials containing such radicals are sulfonated styrene-divinyl benzene copolymers, terpolymers of maleic acid (or its anhydride) -divinyl benzene-styrene, sulfonated phenol-formaldehyde polymers, and sulfonated or carboxylated crosslinked epoxy resins of the Bisphenol A-epichlorohydrin type.

Preferably, the barrier comprises carboxy substituted organic polymers which are cured or polymerized in situ in a diaphragm material, such as asbestos. In situ polymerization involves the polymerization of a polymer such as maleic anhydride-styrene having a low molecular weight and crosslinking the polymer in the diaphragm with divinyl benzene in the presence of a peroxide catalyst such as benzoyl peroxide, dicumyl peroxide or hydrogen peroxide. Instead of a peroxide catalyst, there may be employed conventional redox catalyst systems or straight organo-sulfonyl or persulfate catalysts. On the other hand, such polymerization may be effected in the presence of the aforementioned catalysts by impregnating the diaphragm with the various reactants such as maleic anhydride or maleic acid with divinyl benzene and/or styrene in a solvent in heating the diaphragm, generally under pressure.

In the electrolysis of an aqueous solution of sodium chromate, as described above, enhanced results in terms of reduced power consumption and extended membrane life in the cell are found when the barrier is an asbestos film impregnated with a polymer made from the polymerization of maleic acid or anhydride with another olefinically unsaturated monomer, such as divinyl benzene and/or styrene. Thus, the polymer may be a copolymer of maleic acid or anhydride and divinyl benzene or a terpolymer of maleic acid or anhydride, divinyl benzene and styrene. It is preferable that the co- or terpolymer be made by the addition polymerization of maleic acid or anhydride in a molar quantity exceeding the total molar quantity of the other olefinically unsaturated comonomers, e.g., divinyl benzene and/or styrene.

The most preferable permionic membrane is an asbestos diaphragm impregnated with a resinous co- or terpolymer of 20 to 50 mole percent maleic acid or anhydride, 10 to 50 mole percent divinyl benzene and 0 to 40 mole percent styrene. It has been found that this polymer gives extended cell life before membrane breakdown.

The aforementioned electrolytic permionic cells are operated by feeding aqueous sodium chromate containing solution to the anode compartment and adding to the cathode compartment water or an aqueous sodium hydroxide solution or an aqueous sodium bicarbonate or carbonate solution. By establishing a current across the electrode, electrolytic decomposition is effected thereby producing sodium dichromate in the anolyte. A variety of products may be produced in the catholyte compartment dependent upon the variants added thereto. For example, if carbon dioxide is added to the catholyte, production of sodium carbonate is effected therein. If only water is added, then only sodium hydroxide is produced. For optimum cell efficiencies, it is desirable to establish in the catholyte chamber a carbonate (CO_3) to sodium ion ratio of 0.03 to 0.49, preferably from 0.08 to 0.42. In this manner there is produced a sodium hydroxide and sodium carbonate mixture in the catholyte chamber. This mixture may be treated according to the process discussed in copending application Serial No. 136,312, filed September 6, 1961. Said copending application discloses a method for the production of alkali metal carbonate, alkali metal bicarbonate and alkali metal sesquicarbonate.

The temperature of electrolysis may be from 30 to 90° C., preferably from 65 to 80° C. No criticality has been found in the current densities or voltages applied in regard to adverse effects in producing sodium dichromate.

Reference is made to FIGURE 1, which is an exploded isometric view of a permionic membrane containing electrolytic cell in which the aforementioned electrolytic process is readily effected.

Referring to FIGURE 1, anode **100**, which may be a steel blade coated with lead or a solid lead blade, is separated from spacer **103** by gasket **102** having the exact shape of spacer **103**. In the back of spacer **103** is membrane **104**. This membrane is a rectangular sheet having the same rectangular area as anode blade **100**. Separating membrane **104** from cathode screen **101** is gasket **105** and spacer **106** in the order characterized in FIGURE 1. Gaskets **113** are employed for backing the anode and screened cathode. Electrolytic connections at **107** and the size of the cathode screen (not shown) are provided in the usual fashion. When the various sections are clamped together into one unitary body, the structure has a hollow interior which is characterized by the rectangular hollow of the spacer. This hollow interior extends from the anode to the cathode except for the presence of the blocking membrane. Thus, the membrane establishes an anode compartment and a cathode compartment wherein the liquids may flow separated from each other in each of the chambers.

Inserted in the bottom of spacer **103** is outlet pipe **108** for removal of anolyte liquor. Anolyte overflow pipe **109** serves to maintain the proper anolyte liquor level in the cell. Pipe **114** inserted in the side of spacer **103** provides an opening to the cell's interior for the introduction of chromate solution to the cell. Thus, the sodium chromate is introduced through pipe **114** to the anode compartment of the cell. Inserted in the top of spacer **103** is oxygen outlet pipe **115**. In the cathode compartment of the cell is catholyte liquor removal pipe **110**, water inlet pipe **112** and hydrogen outlet pipe **111**, all of which are inserted in spacer **106** to make an open connection with the cathode compartment of the cell.

The cell unit described above may be utilized as a single unit of a multi-compartmental bipolar cell. Thus, a plurality of the units inserted back-to-back in a cell operates effectively in large scale production of chromic acid. Such a cell is described in copending application of Sydney Forbes, Serial No. 848,430, filed October 23, 1959, now abandoned.

The following example describes a specific operation of the aforementioned process.

Example

An electrolytic cell substantially the same as in the drawing, wherein rubber gaskets **113** were 6-inch x 8-inch, anode **100** was an 8-inch x 10-inch x ⅛-inch sheet of mild steel coated with lead, and cathode **101** was an 8-inch x 10-inch steel screen, was employed to effect electrolysis. Spacers **103** and **106** were rectangular in shape and had an 8 inch x 10 inch area and were ⅝-inch thick. Carved out of the interior of both spacers was a 4-inch x 6-inch space giving 24 square inches of area. The spacers were made of polyvinyl chloride. Pipes **108**, **109**, **110**, **111**, **112**, **114** and **115** had a ⅜-inch internal diameter and were positioned in the cell as described above and illustrated in the drawing. Membrane **104** was a poly-

mer impregnated sheet of crocidolite asbestos saturating paper.

The membrane was formed by immersing the paper in a monomer solution, described below, draining the excess solution and then placing the saturated paper between two plates of glass. The glass plates were sealed with masking tape and further sealed with a cellulosic pressure-sensitive adhesive tape so as to prevent escape of solution or vapor from the impregnated paper. The sealed plates containing the membrane was put in an oven at 70° C. for 4 hours. Before the membrane was put into a cell, it was hydrolyzed in 250 grams per liter aqueous sodium hydroxide solution for 16 hours.

The monomer solution was prepared as follows: A solution of styrene and divinyl benzene was passed through a bed of calcium sulfate thereby removing the inhibitors contained therein. Maleic anhydride was slowly added to an inhibitor-free solution of divinyl benzene and styrene in dioxane. After all of the maleic anhydride was dissolved in the solution, dichlorobenzoyl peroxide was added. The molar quantity of maleic anhydride was twice that of the combined molar quantity of divinyl benzene and styrene employed in the solution. On a basis of the weight of solution, maleic anhydride represented 48.2 percent by weight, divinyl benzene represented 17.5 percent by weight (using a 54.3 percent by weight divinyl benzene mixture with, for example, ethyl benzene), styrene was present in the solution at 3 percent by weight and dioxane was present at 30.3 percent by weight of the solution.

This mixture had a pot life of approximately 2 hours at room temperature which could be extended by cooling. For example, the solution is stable for several days when stored in Dry Ice.

Dioxane in the above monomer solution served as a solvent. Polymer loading of the matrix was .340 grams per square inch which represents the amount of polymer in grams per spuare inch loaded on the crocidolite saturating paper.

An aqueous solution of sodium chromate containing 39.29 percent by weight thereof of sodium chromate and 24.25 percent by weight thereof of CrO_3, was fed through pipe 114 to the anode compartment of the cell. Water was introduced to the cathode compartment of the cell. The temperature of the chromate solution prior to introduction into the cell was 30° C. A current of 21 amps was introduced to the cell giving a current density of 0.87 amp per square inch. The voltage drop in the cell was 3.72 volts.

The sodium chromate solution was continuously added to the cell during the electrolysis at a rate so that the amounts of anolyte in the cell remained at a constant amount, that is, 0.6 liter. Addition of this solution to the cell after the initial feed was held back until the anolyte in the anode compartment of the cell had a pH below 5.

The cell was operated at various pH levels and the anolyte was sampled at these various levels to determine the concentration of sodium chromate, sodium dichromate and chromic acid. It was found that when the pH of the anolyte was below 1.5 that no sodium chromate was present in the anolyte and the chromic acid concentration rose as high as 17.4 percent by weight of the anolyte. When the pH of the anolyte exceeded 5, the sodium chromate concentration typically exceeded 1 percent by weight of the anolyte product and at a pH of 6.2 it was found that the sodium chromate concentration exceeded 10 percent by weight of the anolyte. When the pH of the anolyte on removal from the cell was above 1.5 and below 4.5, the sodium chromate concentration fell below 1 percent by weight of the anolyte and the chromic acid concentration, determined as CrO_3, fell below 0.4 percent by weight of the anolyte. When the pH of the anolyte was above 2.5 and below 4.5, sodium chromate concentration fell below 1 percent by weight and the chromic acid concentration fell below 0.05 percent by weight of the anolyte. When the pH of the anolyte was held between 2.5 and 4, the sodium chromate concentration was below 0.2 percent by weight and the chromic acid concentration fell below 0.05 percent by weight thereof. At a pH of 3.0 the anolyte obtained was essentially free of sodium chromate and chromic acid and contained 100 percent sodium dichromate, basis chromate weight in anolyte.

Comparable results were obtained when an aqueous solution of sodium chromate obtained from the roasting of chrome ore as described above was fed to the anode compartment of the above-described cell.

The sodium hydroxide produced in the cathode compartment in the above example was, in all cases, essentially free of chromium as chromic acid or chromate. The sodium hydroxide solution produced in the cathode compartment had less than 0.01 percent by weight of NaCl, less than 0.01 percent by weight of Si and less than 0.001 percent by weight of manganese, nickel, magnesium, chromium, iron, aluminum, calcium and copper ion impurities (basis combined weight of these impurities), each value based on the weight of the caustic solution.

Although the above discusses this invention in relation to a variety of specific details, the invention is not limited thereto except insofar as they are recited in the claims.

I claim:

1. A process for producing sodium dichromate which comprises feeding an aqueous solution of sodium chromate having a CrO_3 content of between 50 to 550 grams per liter to the anode compartment of an electrolytic cell having an anode and a cathode compartment, providing in said cell a permionic membrane which divides the cell into two sections, one section containing the cell anode, the other section containing the cell cathode, said permionic membrance being impervious to the passage of chromate ions, feeding water to the cathode section of said cell, electrolyzing the cell contents and withdrawing anolyte from the anode section of the cell when the pH of that anolyte reaches a value between 1.5 and 5.

2. In a process of producing sodium dichromate by the electrolysis of sodium chromate in an electrolytic cell having an anode and a cathode compartment, said compartments being separated by a permionic membrane which is impervious to the passage of chromate ions, the steps comprising feeding sodium chromate to the anode compartment of said cell and water to the cathode compartment, passing a current to the cell and removing the liquor formed in the anode compartment when the pH of said liquid falls between 1.5 and 5.

3. A process for producing sodium dichromate by the electrolysis of sodium chromate in an electrolytic cell having an anode and a cathode compartment, said anode and cathode compartments being separated by a permionic membrane which is impervious to the passage of chromate ions, comprising feeding sodium chromate to the anode compartment of said cell and water to the cathode compartment, passing a current to the cell and removing the liquor formed in the anode compartment when the pH falls between 3 and 5.

4. A process for producing sodium dichromate in an electrolytic cell having an anode and a cathode compartment and having a permionic membrane separating said anode and cathode compartment, said membrane being impervious to the flow of chromate ions, comprising feeding the sodium chromate to the anode compartment of said cell and water to the cathode compartment passing a current to the cell and removing the liquor formed in the anode compartment at a pH of between 2.5 and 3.5.

5. The process of claim 2 wherein the sodium chromate is added in aqueous solution.

6. The process of claim 3, wherein the sodium chromate is added in the form of an aqueous slurry.

7. The process of claim 2 wherein the permionic membrane in said cell comprises asbestos impregnated with a polymer of maleic acid and another unsaturated monomer.

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