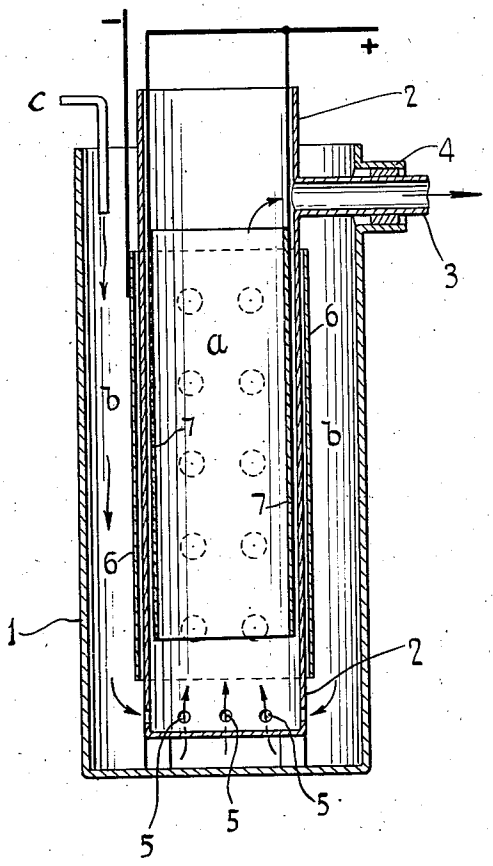
Sept. 29, 1942. H. SCHMIDT 2,297,252

PROCESS FOR THE PURIFICATION OF SOLUTIONS THAT SERVE AS GENERATORS FOR PERCOMPOUNDS

Filed June 17, 1938



INVENTOR
HEINRICH SCHMIDT
BY
Hammond & Littell
ATTORNEYS

Patented Sept. 29, 1942 2,297,252

UNITED STATES PATENT OFFICE

2,297,252

PROCESS FOR THE PURIFICATION OF SOLUTIONS THAT SERVE AS GENERATORS FOR PERCOMPOUNDS

Heinrich Schmidt, Niederskunnersdorf, Germany; vested in the Alien Property Custodian

Application June 17, 1938, Serial No. 214,245
In Germany February 12, 1937

5 Claims. (Cl. 204—84)

This invention relates to a process and apparatus for the electrolytic reoxidation of solutions used in the production of hydrogen peroxide. More particularly it relates to a process for the purification and reoxidation of solutions used in a cyclic process for the production of hydrogen peroxide.

In a cyclic process of producing hydrogen peroxide by the distillation of solutions containing persulfuric acid or persulfate, the residual liquor remaining after distillation contains valuable constituents and is, therefore, returned to electrolytic cells for reoxidation to persulfuric acid or persulfate as the case may be. However, as the residual liquor obtained after such distillation also contains impurities, such as Caro's acid (H_2SO_5), hydrogen peroxide itself and metallic impurities which act as catalysts, it has not previously been possible to carry out this reoxidation in a simple diaphragmless cell in which both anode and cathode are in a common chamber. Therefore, in prior practice it has been necessary to use cells in which the cathode and anode are in separate chambers and to pump or otherwise cause the electrolyte to flow through the anode chamber after its passage through the cathode chamber. This prior practice is objectionable because diaphragm cells are not only more difficult to operate but are more expensive both in initial cost and operating cost due to a greater power consumption.

The principal object of the present invention is to provide a process by which the residual solution obtained after distilling off the hydrogen peroxide may be purified sufficiently to permit its efficient reoxidation in a simple diaphragmless cell.

Another object is to provide a process for the reoxidation of the residual solution obtained after distilling off the hydrogen peroxide in accordance with which the harmful impurities are removed at the cathode without substantially affecting the concentration of the solution and in accordance with which the same current used for the purification is utilized at the anode for the partial oxidation of the solution.

A further object of this invention is to provide a suitable cell in which this process may be carried out efficiently.

Other objects will become apparent from a consideration of the specification and the claims appended thereto.

The present invention contemplates the treatment of the residual solution obtained as a result of the distillation of solutions of persulfuric acid and persulfates for the purpose of obtaining hydrogen peroxide therefrom.

In accordance with the process of the present invention the residual solution obtained as a result of the distillation step, after its usual dilution to the proper concentration, is first subjected to a cathodic reduction to free the solution from impurities such as Caro's acid, hydrogen peroxide, metallic catalytic impurities and the like which detrimentally affect reoxidation and thereafter reoxidized in one or more simple diaphragmless cells to obtain for redistillation a solution containing the desired amount of persulfuric acid or persulfate.

The cathodic potential most suitable for purification is obtained by a careful selection of cathode material, current density, cell resistance and speed of flow of the solution. As the residual solution usually contains a small amount of persulfate the most suitable potential is preferably such that the impurities are reduced without appreciable reduction of the persulfate. The reduction itself is, therefore, carried out without any substantial change of concentration of persulfate with the result that the subsequent loss of oxygen during distillation is minimized. In most instances it is desirable to pass the solution which has been reduced in the cathode chamber through the anode chamber of the same cell, thereby utilizing the full energy of the cell and reoxidizing the solution to some extent depending upon the conditions existing therein. However, it is to be understood that this reoxidation may be omitted if desired, in which case the purified solution leaving the cathode chamber is directly passed into the diaphragmless cells for oxidation therein.

It is also to be understood that the solution may be purified by passing it through the cathode chambers of a number of cells in series, and then if desired through the anode chambers of the cells.

The cathode chamber of the diaphragm cell in which the purification takes place may be of any desired construction or design. For example, a diaphragm in the form of plates or the like may be built into the cell container to separate the two chambers. A cell particularly adaptable for use is shown in cross section in the accompanying drawing wherein casing 1 made of any suitable material contains a separated concentric cylindrical diaphragm 2, the outlet pipe 3 of which passes through an opening in the container to which it is sealed at point 4. The cylindrical diaphragm 2 forms the enclosure for the cylin-

drical anode chamber *a* which is connected with annular cathode chamber *b* by a series of holes 5 near its bottom. The cathode 6 surrounds the diaphragm 2 inside of which there is an anode 7 also of cylindrical shape. The electrolyte is introduced into the cathode chamber *b* at point *c* and leaves near its bottom by means of the holes 5 entering the anode chamber, flows past the anode 7 and leaves the cell at the outlet pipe 3. Cooling elements of any design or style may be provided in the cell. The electrodes themselves may be provided with internal cooling means.

After purification by cathodic reduction in the diaphragm cell, the solution is oxidized to the desired extent in a simple diaphragmless cell or a series of such cells.

As a direct result of the present invention, it is possible for the first time to use simple diaphragmless cells employing a single chamber for both anode and cathode for the reoxidation of solutions from which a good yield of hydrogen peroxide may be distilled. This method is simpler than those which have previously been used in the cyclic process for producing peroxide from persulfate solutions.

In the following examples, a typical process of the prior art is contrasted with a preferred embodiment of the process of this invention. Four thousand liters of a solution containing 220 grams per liter of ammonium sulfate and 300 grams per liter of sulfuric acid are oxidized to persulfate solutions in a continuous manner using well-known cells in which the anode and cathode are located in a common chamber. This oxidation is carried out in such manner that the current flows through the cells at the rate of 15,000 amperes per minute and the electrolyte leaves the cells containing about 34 grams per liter of the peroxide as persulfate. This solution is then conducted in a continuous manner to the usual distillation apparatus used for the decomposition of persulfate solutions and the separation of the peroxide where it is distilled. The resultant residue is then diluted with water and brought back to the initial concentration of 300 grams per liter of sulfuric acid and re-electrolyzed. When this method is used, the electric efficiency based on peroxide recovered by distillation is about 40% at the start and gradually falls to 35% or less as the operating time increases. However, if purification equipment such as described herein is inserted in the above cyclic process between the distillation and the re-electrolysis, it is possible to obtain yields of 56–65%.

In accordance with a preferred embodiment of my invention, the diluted residue is uniformly passed through the cathode chambers of four cells in parallel and electrolyzed in each cell with a current of 2 amperes using a cathode current density of 0.01–0.02 ampere per square centimeter and an anode current density of 1.0 ampere per square centimeter at a temperature not above 20° C. Upon leaving the purification cells, the electrolyte which contains persulfate is immediately passed into the diaphragmless cells mentioned in the previous example. The solution leaving these cells contains 34 grams per liter of peroxide in the form of persulfate. In making the calculation of the above yields of 56–65%, the total electric energy put into the process, that is that made use of in the purification cells, is also included. The high yield obtained in this manner remains constant for a long period of time.

The term "persulfate" as used herein includes persulfuric acid as well as the persulfates such as the ammonium, potassium and sodium salts. The reoxidation in the diaphragmless cell may be defined as "exposing the solution to simultaneous anodic oxidation and cathodic reduction to oxidize the solution to obtain the desired concentration of persulfate."

It will be understood that the embodiment of my invention described in this specification and the apparatus illustrated by the drawing is only a preferable form of my invention and I, therefore, desire a broad interpretation of the invention within the scope and spirit thereof and limited only by the claims appended hereinafter.

I claim:

1. In a continuous cyclic process for producing hydrogen peroxide by distillation from a persulfate solution, the steps consisting of diluting the residual solution obtained after said distillation, purifying the diluted solution by passing it through the cathode chamber of at least one diaphragm cell in which the cathode potential is maintained sufficient to reduce the impurities in the solution without appreciably reducing the persulfate present, thereupon partially reoxidizing said solution by passing it through the anode chamber of the diaphragm cell, and then passing the solution leaving the diaphragm cell through at least one diaphragmless cell and completing the reoxidation in said diaphragmless cell by exposing the solution to current conditions effective for anodic oxidation to persulfates of high concentration.

2. A continuous cyclic process for electrolytically producing hydrogen peroxide by distillation from a persulfate solution, comprising distilling off the hydrogen peroxide therefrom, diluting the residual liquid, purifying the diluted liquid by subjecting it to cathodic reduction in the cathode chamber of at least one diaphragm cell in which the cathode potential is maintained sufficient to reduce the impurities in the solution without appreciably reducing the persulfate present, and subsequently reoxidizing the so purified liquid by passing it through at least one diaphragmless cell wherein it is exposed to current conditions effective for anodic oxidation to persulfates of high concentration.

3. In a continuous cyclic process for producing hydrogen peroxide by distillation from persulfate solutions, the steps comprising diluting residual solutions obtained after said distillation, purifying said solutions by introducing them into at least one diaphragm cell, causing said solutions to flow downwardly through the outer cathode chamber of said cell, into an inner anode chamber, and upwardly through the latter, and freeing said solutions during the passage through the cathode chamber of impurities by electrolytic reduction at a cathode potential maintained sufficient to reduce the impurities in the solutions without appreciably reducing the persulfate present, and subsequently oxidizing the solutions leaving the diaphragm cell by passing them through at least one diaphragmless cell wherein they are exposed to current conditions effective for anodic oxidation to persulfates of high concentration.

4. In a continuous cyclic process for producing hydrogen peroxide by distillation from persulfate solutions, the steps comprising diluting residual solutions obtained after said distillation, purifying said solutions by passing them through at least one diaphragm cell by introducing the solutions into the top of a cathode chamber sep-

arated from the anode chamber by a diaphragm, causing the solutions to flow downwardly through the cathode chamber and into the anode chamber through a connecting passage at the bottom of the diaphragm cell, causing the solutions to flow upwardly through the anode chamber and to leave the diaphragm cell at the top, freeing said solutions in their flow through the cathode chamber of impurities by electrolytic reduction at a cathode potential maintained sufficient to reduce the impurities in the solutions without appreciably reducing the persulfate present, and subsequently passing the solutions leaving the diaphragm cell through at least one diaphragmless cell, and reoxidizing said solutions in said diaphragmless cell by exposing the solutions to current conditions effective for anodic oxidation to persulfates of high concentration.

5. In a continuous cyclic process for the production of peroxide from percompounds by distillation, the steps comprising purifying residual solutions obtained after said distillation by removing electrode poisons by means of a preliminary electrochemical treatment, said treatment comprising subjecting the solutions to cathodic reduction in a cathode chamber of at least one diaphragm cell in which the cathode potential is maintained sufficient to reduce the impurities in the solutions without appreciably reducing the persulfate present by passing the solutions downwardly through the cathode chamber of a cell communicating near the bottom with an anode chamber, causing the solutions to flow through the cathode chamber into the anode chamber, subjecting the solutions to a preliminary oxidation while the same are flowing upwardly through said anode chamber, causing the solutions to leave the diaphragm cell from the top of the anode chamber, and then passing the solutions leaving the diaphragm cell through at least one diaphragmless cell wherein the reoxidation is completed by exposing the solutions to current conditions effective for anodic oxidation to percompounds of high concentration.

HEINRICH SCHMIDT.