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ELECTROLYTIC PROCESS OF PREPARING ARSENATES

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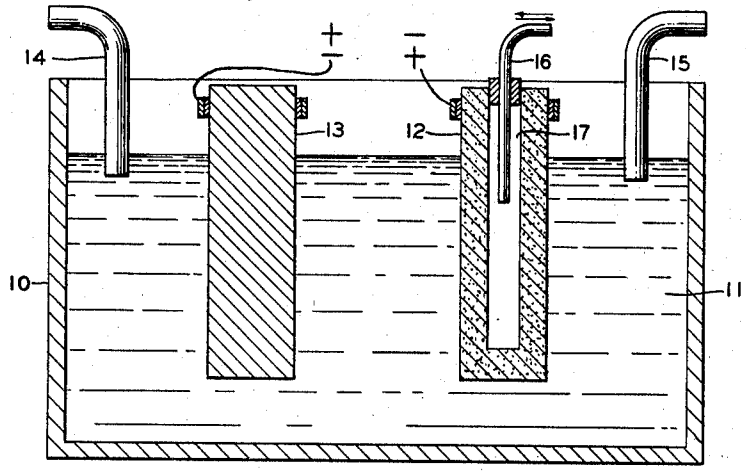


FIG. 1

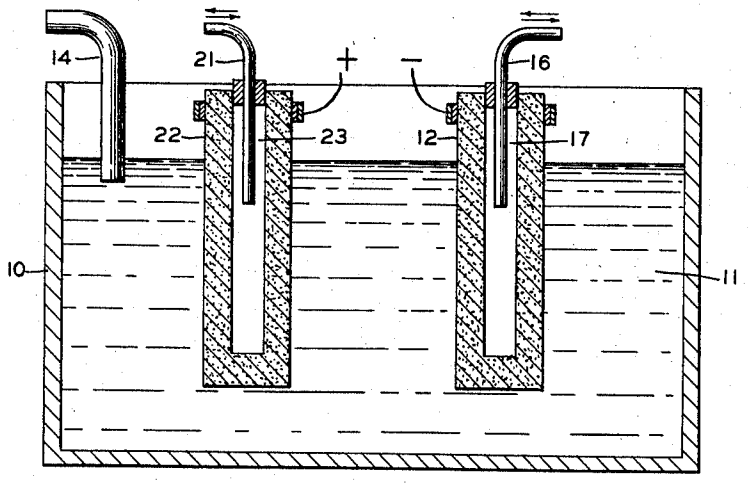


FIG. 2

INVENTORS
GEORGE W. HEISE
MILTON JANES
BY E. E. Greenewald
ATTORNEY

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ELECTROLYTIC PROCESS OF PREPARING ARSENATES

Milton Janes, Lakewood, and George W. Heise, Rocky River, Ohio, assignors to National Carbon Company, Inc., a corporation of New York

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7 Claims. (Cl. 204—86)

This invention relates to an electrolytic process in which an impressed electric current is passed through a cell having insoluble electrodes immersed in an aqueous electrolyte. More specifically, the invention is a process for electrolytically oxidizing a water soluble arsenite, such as sodium or other alkaline metal arsenite, to the corresponding arsenate.

It has heretofore been proposed to oxidize arsenites, obtained for instance by dissolving arsenious oxide in an alkaline solution, to arsenates by anodic oxidation at a solid anode according to the reaction:

$$Na_3AsO_3+H_2O+(2F)=Na_3AsO_4+H_2$$

High current efficiency has been attained only by the use of diaphragms which increase the operating voltage, of low current density, and of agitation of the solution. Formation of elemental arsenic at the cathode involves a loss of product and tends to foul the diaphragms. Current efficiency decreases with decreased concentration of arsenite, and batch operation has been customary.

It is an object of this invention to provide a continuous process for oxidizing arsenites to arsenates at a high current efficiency. A further object is to lower the operating voltage in such a process. Another object is to make possible the elimination of diaphragms in the process. Still another object is to provide a process in which a high percentage conversion of arsenite to arsenate is attained. Another object is to provide a process of the kind described wherein high current densities may be used at the anode without seriously lowering either the current efficiency or the percentage conversion of arsenite to arsenate.

Other objects of the invention include the provision of a process in which deposition of elemental arsenic is avoided, and in which arsenate is produced at the cathode as well as at the anode.

These and other objects of the invention are attained by a process in which a porous carbonaceous anode is used. In one embodiment of the invention a nonporous insoluble cathode is used; in another embodiment the cathode is porous and carbonaceous.

The invention will be more particularly described with reference to the accompanying drawing in which:

Fig. 1 represents diagrammatically in vertical cross-section an electrolytic cell container 10 containing an aqueous electrolyte 11 in which are immersed a porous carbonaceous anode 12 and a nonporous cathode 13, and

Fig. 2 represents diagrammatically in vertical cross-section an electrolytic cell similar to that shown in Fig. 1 except that it contains two porous electrodes 12 and 22.

In accordance with one application of the invention, illustrated by Fig. 1, electrolyte 11 containing dissolved arsenite is electrolyzed by passage of electric current between a cathode 13 and a porous carbonaceous anode 12, whereby arsenate is formed at the anode. Anolyte containing the arsenate is removed continuously from the cell 10 through the porous anode 12 as it is formed, and arsenite is fed to the cell 10 from time to time or continuously. Diffusion of arsenate into the main body of the electrolyte 11 may thus be prevented more or less completely. Evolution of oxygen may be avoided, high current densities may be employed, and a low operating cell voltage is obtained.

It will ordinarily be desirable to use a diaphragm to isolate the catholyte in this application of the invention.

During continuous or prolonged operation of the cell, the electrolyte composition remains unchanged, a uniform high concentration of arsenite is maintained at the active electrode surface, and both a high current efficiency and a high percentage conversion are obtained.

In an alternative embodiment, alkaline electrolyte containing the arsenite may be introduced into the cell 10 through the porous anode 12.

In actual practice of the above-described embodiment of the invention, current densities as high as 100 amperes per square foot of anode superficial area have been used successfully, and even at this current density an overall current efficiency of 92% to 99% and a 90% conversion of sodium arsenite to sodium arsenate have been maintained.

In typical experiments a solution containing 40 grams of arsenious oxide and 54 grams of sodium hydroxide per liter was electrolyzed at 28° C. and at an anode current density of 14 amperes per square foot. Using a nonporous graphite anode and an iron cathode the cell operating voltage was 3.17; whereas when a porous graphite anode and an iron cathode were used the cell operating voltage was 2.45. In each instance, a single diaphragm was used.

Because of the high conversion efficiency, sodium arsenate may be continuously produced from the arsenite without recirculating the electrolyte solution.

Although various materials may be used more or less successfully as the anode 12, we prefer a

carbonaceous material having a porosity above 35% (preferably between 40% and 70%), calculated as follows: Percent porosity=100 (real density—apparent density) ÷real density; and an air permeability above 15, preferably above 30. Whenever used herein and in the appended claims, the term "air permeability" means the number of cubic inches of air per minute passing through one square inch cross-section of electrode material, when air at a pressure of one pound per square inch is blown through a block of the material one inch thick. The following table shows, for purposes of comparison, the porosity and permeability of ordinary electrode carbons (Types 1, 2, and 3) and of the special electrode carbons preferably used in the process of this invention (Types 4, 5, 6, and 7).

Type	Percent porosity	Air permeability
1	25	2
2	28	7
3	33	2
4	60	20
5	57	30
6	40	120
7	42	600

We have also found that the pores of the anode material should be relatively minute and uniformly distributed, and not large, scattered voids and fissures. Material having the latter kind of pores might be described as "leaky" rather than "porous." The relative uniformity of distribution of the pores in the two kinds of materials may be distinguished by a simple test: if air is forced through a thin block of the material under water, at about the minimum air pressure required to obtain bubbles in the water, the "porous" material gives forth a cloud of small bubbles over its entire surface, while the "leaky" material gives a number of separate streams of bubbles issuing from the larger fissures and voids.

Another test for uniformity of porosity of these materials comprises determining the flow of a viscous liquid, such as a concentrated aqueous solution of cane sugar, under a moderate pressure, for instance a head of about six inches, through a thin (e. g. one-eighth inch) section of the material. Any relatively large fissures permit flow of the solution and are thereby made evident.

Porous anode material for use in the process of this invention may suitably be made from comminuted solid carbonaceous material (for example, coke, graphite, or charcoal) and a porous carbonaceous binder (for instance, baked tar or pitch). Suitable methods for making such electrode material are described in U. S. Patent 1,988,478, issued on January 22, 1935, to B. E. Broadwell and L. C. Werking.

If the process of the invention is operated as described above, some metallic arsenic is deposited at the cathode by a side reaction:

$$5Na_3AsO_3+3H_2O+(6F)=\underline{2As}+3Na_3AsO_4+6NaOH$$

Arsenic so deposited is spongy and spreads through the solution unless a diaphragm is used. Its production is not only a waste of material; it also tends to foul the porous anode or diaphragm.

The deposition of arsenic is prevented in an alternative embodiment of the invention, illustrated by Fig. 2, wherein a porous carbonaceous cathode 22 is employed and a cathodic depolarizer is introduced into the cell through the cathode.

A suitable cathodic depolarizer is air blown through the cathode, and the oxygen of the air may be used very effectively for depolarization if the cathode is made of carbonaceous material of the type used as electrodes in air-depolarized primary galvanic cells. Material of this type is disclosed for instance in U. S. Patent 2,010,608 issued August 6, 1935, to Erwin A. Schumacher, et al. A cathode of material of this kind may, if desired, be made repellent to electrolyte; several methods of achieving this object are well known.

Depolarization of the cathode with oxygen maintains the cathode potential at a level lower than that at which elemental arsenic can be deposited, thereby making feasible the complete elimination of diaphragms. The reduction in cathode potential and the elimination of diaphragms decrease the operating voltage of the cell more than fifty per cent.

If a moderate current density is used, the cathode potential may be kept low enough to permit chemical oxidation of arsenite to arsenate at the cathode, thereby producing more than 100% of the theoretical yield of arsenate product based on electrical current consumption alone.

In typical experiments using a porous graphite anode and an air-depolarized carbon cathode, a solution containing 40 grams of arsenious oxide and 54 grams of sodium hydroxide per liter was electrolyzed at about 30° C. At an anode current density of 14 amperes per square foot the cell operating voltage was 0.92, and at an anode current density of 28 amperes per square foot the cell voltage was 1.37. Current efficiencies 103% to 168% of theoretical were attained, and arsenite to arsenate conversions of 57% to 90%.

It is ordinarily advantageous to pass material through the respective porous electrodes at at least that rate which is required to supply that amount of reactant, which can theoretically be acted upon by the current used, and a greater rate is usually preferable. For example, it is obvious that with an air depolarized cathode, enough oxygen must be provided to permit chemical oxidation as well as cathodic depolarization, and a rate several hundred per cent the electrochemical requirement may be desirable.

It will readily be understood that the specific descriptions of operating conditions disclosed herein are only by way of example, and that the invention is not limited to such specific examples.

We claim:

1. Method of oxidizing a water soluble arsenite to the corresponding arsenate which comprises passing an electric current through an aqueous electrolyte, containing said arsenite, between a cathode and a porous anode, whereby the arsenite is oxidized to arsenate at said anode, and promptly withdrawing through the pores of said anode anolyte containing said arsenate.

2. Method of oxidizing a water soluble arsenite to the corresponding arsenate which comprises passing an electric current through an aqueous electrolyte, containing said arsenite, between a cathode and a porous anode, whereby the arsenite is oxidized to arsenate at said anode, and promptly withdrawing through said anode anolyte containing said arsenate; said porous anode

having a porosity above 35% and an air permeability above 15 and comprising comminuted solid carbonaceous material and a porous carbonaceous binder having uniformly distributed pores.

3. Method of oxidizing sodium arsenite to sodium arsenate which comprises passing an electric current through an aqueous electrolyte, containing sodium arsenite, between a cathode and a porous anode, said anode having a porosity between 40% and 70% and an air permeability above 30 and comprising comminuted solid carbonaceous material and a porous carbonaceous binder having uniformly distributed pores, whereby sodium arsenite is oxidized to sodium arsenate at the porous anode, and continuously withdrawing through said porous anode anolyte containing said sodium arsenate.

4. Method of oxidizing a water soluble arsenite to the corresponding arsenate which comprises passing an electric current through an aqueous electrolyte, containing said sodium arsenite, between a porous cathode and a porous anode of an electrolytic cell, passing a cathodic depolarizing fluid through the porous cathode into the cell, and removing through the pores of said anode anolyte containing sodium arsenate.

5. Method as defined in claim 4, wherein the cathode is composed of material capable of depolarization by air and the depolarizing fluid is air.

6. Method of oxidizing sodium arsenite to sodium arsenate which comprises passing an electric current through an aqueous electrolyte, containing sodium arsenite, between a porous cathode and a porous anode of an electrolytic cell, said porous cathode being composed of carbonaceous material capable of depolarization by air and said cathode and anode having a porosity between 40% and 70% and an air permeability above 30 and comprising comminuted solid carbonaceous material and a porous carbonaceous binder having uniformly distributed pores, passing air through said cathode into the cell, and continuously removing through said anode anolyte containing sodium arsenate.

7. Method of oxidizing a water soluble arsenite to the corresponding arsenate which comprises passing an electrolyte containing said arsenite through a porous anode of an electrolytic cell containing said anode and an air depolarizable porous carbon cathode, passing air through the porous carbon cathode into the cell in an amount sufficient to depolarize the cathode, and passing an electric current through said anode and cathode.

MILTON JANES.
GEORGE W. HEISE.