Oct. 11, 1966 E. M. NELSON 3,278,410

ELECTROLYTIC ANODE

Filed May 1, 1962 2 Sheets-Sheet 1

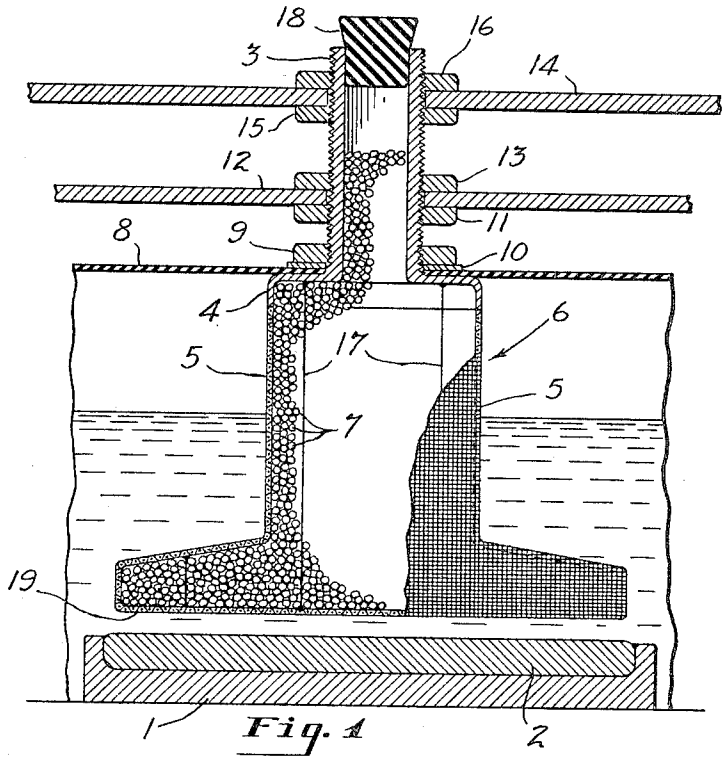


Fig. 1

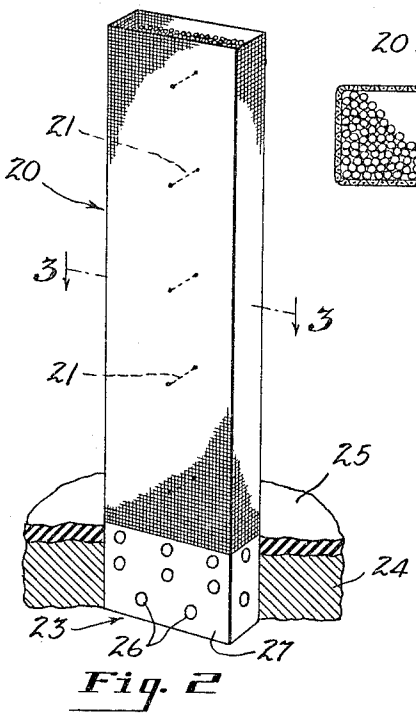


Fig. 2

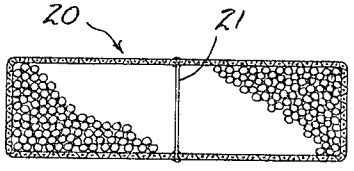


Fig. 3

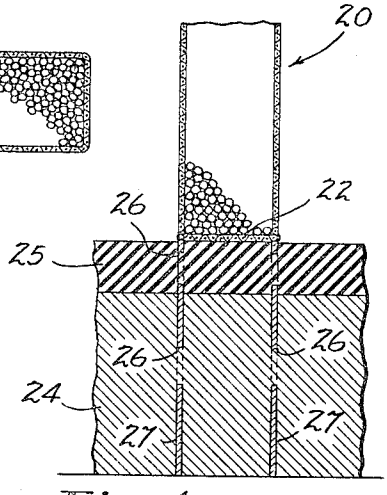


Fig. 4

INVENTOR.
Edwin M. Nelson
BY John Mahoney
ATTORNEY

Oct. 11, 1966 E. M. NELSON 3,278,410

ELECTROLYTIC ANODE

Filed May 1, 1962 2 Sheets-Sheet 2

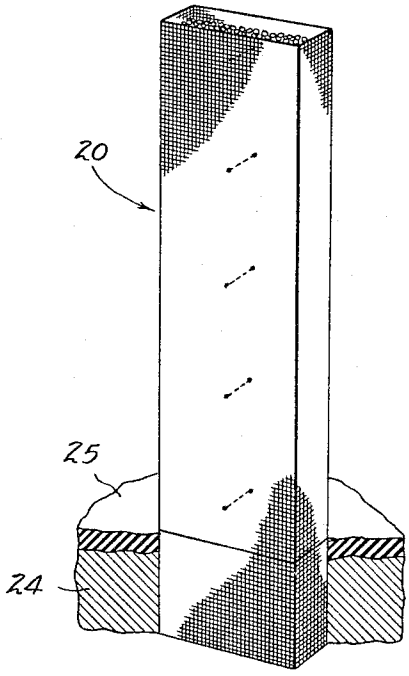


Fig. 5

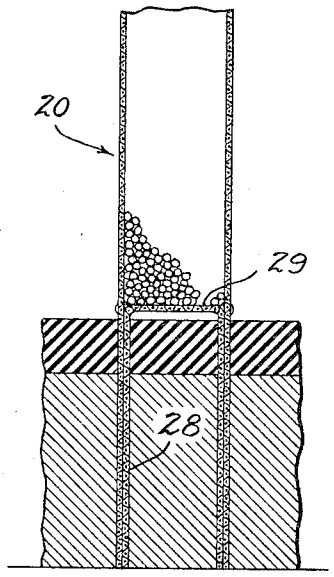


Fig. 6

INVENTOR.
Edwin M. Nelson
BY John Mahoney
ATTORNEY

United States Patent Office 3,278,410 Patented Oct. 11, 1966

3,278,410

ELECTROLYTIC ANODE

Edwin M. Nelson, 1435 Warren Road, Lakewood, Ohio

Filed May 1, 1962, Ser. No. 191,640
11 Claims. (Cl. 204—285)

The present invention relates to electrolytic anodes for use in electrolyzing salts in which chlorine or a radical containing chlorine is formed at the anode.

Anodes which have heretofore been utilized in electrolyzing salt solutions, such as an aqueous solution of sodium chloride, to provide chlorine at the anode and sodium at the cathode, usually consist of graphite in the form of blades. It has also been proposed to utilize titanium which is coated with platinum or a member of the platinum family in place of the conventional graphite anode blades.

Graphite in the form of blades, however, is not very satisfactory because during electrolysis, they gradually wear away which increases the gap between the anode and cathode and necessitates a higher cell voltage. They also have the disadvantage of producing carbon dioxide which passes off with the chlorine and exists as an impurity therein.

When platinum or platinum-coated titanium is utilized as the anode, chlorine of a comparatively high purity may be obtained. Platinum, however, is expensive and during electrolysis, there is a gradual loss of the platinum. Likewise, when platinum-coated titanium is utilized as the anode, the platinum not only is chemically attacked but it has the tendency to strip from the titanium. Platinum or platinum-coated titanium is also objectionable because it cannot readily be substituted for the blade graphite in present diaphragm cells.

In accordance with the present invention, I have provided an improved electrolytic anode including a screen basket which is formed of a metal that is strong but which becomes passivated when subjected to the electrolyzing bath, such as titanium, to which current is conducted from a positive source of electrical energy. To prevent the titanium from becoming passivated, however, I coat the inner side or both sides of the titanium with platinum or a member of the platinum family, and then fill the interior of the screen housing with anode particles. When the titanium screen housing is coated on one or both sides with platinum and the housing is filled with anode particles, such as graphite particles, because of the increased anode area, the voltage at the anode will be lower than when platinum-coated titanium is utilized alone as the anode and consequently there will be less loss of the platinum by chemical means and less stripping of the platinum from the titanium than in platinum-coated titanium anodes. The anode particles enclosed within the screen housing must be electrically conductive and resistive to corrosion by the electrolyte and although I do not desire to be limited to the shape of the anode particles, small graphite particles which are spherical in shape or which have one or more round surfaces are especially desirable because in such case the chlorine formed at the anode passes rapidly from between the particles and does not block the active anode surface. When the particles have rounded surfaces or are spherical in shape, there is also less wearing away of the particles and consequently less sludge is formed.

It will also be apparent that in my improved anode, a substantial portion of the chlorine is formed at the graphite particles and consequently there is a substantial saving in the amount of platinum used. When graphite particles are utilized, a greater anode area is also provided which lessens the current density at the anode and consequently there will not only be less loss of the platinum by chemical means but there will be less stripping of the platinum from the titanium. Because the graphite particles, irrespective of their shape, have large openings around them, it is also apparent that the electrolysis takes place at deeper surfaces within the anode particles than when the conventional graphite blades are utilized as the anode and consequently a lower anode voltage results because of the greater anode surface.

Another particular advantage of my improved anode is that it may be incorporated in diaphragm cells now in commercial use without change or with only a minimum change to the cell and in cells of the horizontal mercury type, such as the De Nora cell, a higher current density may be provided than when graphite blades are utilized because, due to the rapid removal of the chlorine from the graphite particles in my improved anode, there is always a large effective anode area.

It is therefore an object of the present invention to provide an electrolytic anode which has a large surface with a corresponding low voltage, which has a comparatively long life, and which possesses all of the advantages of a platinized-titanium anode but which is less costly because there is less loss of platinum in my improved anode than in a platinized-titanum anode alone.

Another object of my invention is to provide an electrolytic anode containing graphite particles for producing chlorine or a radical containing chlorine which is in a comparatively pure state.

Other objects and advantages of the invention will become apparent as the specification proceeds.

My invention will be better understood by reference to the accompanying drawings in which:

FIG. 1 is a diagrammatic view of my improved anode and showing in elevation a cathode for use with the anode;

FIG. 2 is an isometric view of another form of my invention.

FIG. 3 is a cross sectional view taken on a plane passing through the line 3—3 of FIG. 2;

FIG. 4 is an enlarged sectional view of the lower portion of the anode shown in FIG. 2;

FIG. 5 is a view similar to FIG. 2 of another form of my improved anode; and

FIG. 6 is an enlarged cross sectional view of the lower portion of the anode shown in FIG. 5.

In FIG. 1 of the drawing, my improved electrolytic anode is shown embodied in a De Nora horizontal mercury cell. This type of cell is shown in FIGS. 91 and 92, pages 271 and 272 of Electrochemical Engineering by Mantell, fourth edition, published byMcGraw-Hill Book Company, New York City, in 1960, in which the graphite is in the form of blades and in which the cathode consists of a steel trough **1** containing mercury **2** with which the electrolyte is in contact. As shown in the drawing, the anode includes a threaded metal tube **3** which is welded or otherwise secured to a flange **4** which is formed of titanium or other passivating metal and the flange **4** in turn is welded or otherwise secured to a screen **5** formed of a passivating metal, such as titanium which forms the housing **6** for graphite **7** which may be in the form of broken graphite particles but which is preferably in the form of particles having rounded surfaces, such as spheres.

As shown in FIG. 1, a flexible rubber sheet **8** having an opening therein is passed over the threaded tube **3** in a manner similar to the De Nora cell shown in the above publication. Rubber sheet **8** is held in place by a nut **9** and a washer **10**. Arranged above and in spaced relation to nut **9**, a second nut **11** is threaded on to the threaded tube **3** which forms a support for a bus bar **12** having a threaded opening therein which is threaded on

tube 3 above nut 11 and nut 13 is threaded on tube 3 above bus bar 12 and is tightened to hold the bus bar in place. The bus bar 12 is in electrical contact with a positive source of electrical energy. A support 14 for maintaining the anode in spaced relation to the cathode and which has an opening therein to receive the tube is also threaded on the tube 3 and is maintained in place by nuts 15 and 16. The titanium screen is supported in place by titanium wires 17 which are spaced far enough apart to permit graphite particles which are inserted in the housing formed by the titanium screen to pass to the bottom of the housing.

A passivating metal, such as titanium, cannot be utilized alone as an anode because when an electrical current is passed through an electrolyte containing water, the metal is oxidized or passivated at its surface and is no longer electrically conductive at its surface. To be conductive at its surface, it is therefore necessary to coat the titanium with a metal of the platinum family. A screen formed of titanium wire or an expanded titanium metal is suitable for use in my improved anode and when a screen is specified in the claims it is to be considered as also covering expanded metal. It should be noted, however, that screens of various designs may have variant conductivity in different directions. This must be taken into consideration in constructing the titanium housing.

In accordance with my invention, the platinum coated screen housing is filled with loose electrically conductive, corrosion resistant particulate anode material which particles are preferably partly rounded or are spherical in shape. Graphite in the shape specified is particularly desirable. When graphite particles are utilized, they are molded under high pressure to minimize porosity and then slowly baked and later graphitized. Such anode particles have a distinct advantage over broken graphite particles because there are no sharp edges to be rounded off. They also provide a large number of openings around the spheres which enable the chlorine formed at the anode to pass freely throughout the anode particles.

The metal tube 3 extending above the electrolyte also provides a space in which additional graphite particles may be stored when particles within the housing are partly consumed. When graphite particles erode, mechanical means, not shown, may be provided to agitate the screen and to promote settling of the anode particles within the titanium screen housing. When the eroded particles are small enough they pass through the screen and may be carried away by the stream of mercury from which they may be filtered. The portion of the anode area provided by the graphite particles may therefore be maintained substantially constant. A stopper 18 is provided for the titanium or other passivating metal tube 3 to prevent the escape of chlorine formed at the anode.

In my improved anode, the titanium serves to conduct current from the bus bar 12 to the anode and even when in the form of a screen, it has sufficient strength to support the rounded graphite particles when reinforced by the titanium wires 7. After exposure, however, to the electrolyte during electrolysis, it becomes passivated, that is an oxide film forms thereon which renders it substantially nonconductive at its exposed surfaces. Before being inserted in the electrolyte, the screen is coated by suitable means, such as plating, with a member of the platinum family and particularly platinum. The titanium screen may be coated only on its inner side but is preferably coated on both sides to increase the conductive area of the anode. It is important that the bottom portion 19 of the housing which is preferably flat, shall be provided with a coating of platinum or a member of the platinum family on both sides so as to make good contact between the titanium screen housing and the graphite particles within the titanium screen housing which platinum of course forms part of the anode and aids in forming the chlorine. In the upper area of the plated screen, the platinum serves principally as a source of electrical leakage to the graphite packing and consequently at such areas there is only a slight loss of platinum per ton of chlorine during electrolysis.

The anode shown in FIG. 2 is similar in construction to the anode shown in FIG. 1 but is designed for insertion in a Hooker type cell as shown on page 281 or the Diamond Alkali cell disclosed on page 283 of the above publication and includes an elongated screen housing 20 formed of titanium or other passivating metal which provides a strong screen housing 1 for the anode particles which preferably consist of particles having rounded surfaces, such as spheres. The screen housing is supported or reinforced by the wires 21 which are spaced at a sufficient distance from the sides of the screen to permit the graphite particles to drop to the bottom of the housing which is also formed of a titanium screen 22 which may be formed of cross wires or expanded metal. A rectangularly-shaped member 23 which is formed of sheet titanium is open at its upper and lower ends and is thick enough to pass all the current from conductor 24 which is usually formed of lead and leads through a layer of mastic 25 to the screen 20. Holes 26 formed between the walls 27 permit lead and a mastic material to flow inside of the anode base. The titanium screens 5 and the rectangularly-shaped base 23 are coated on the inside with platinum or they may be coated on both the inside and outside with that metal or a metal of the platinum family. If desired, however, the anode may be further simplified by using an all screen construction including a second screen 28 having an inverted U-shaped bottom as shown at 29 in FIGS. 5 and 6 which is spot welded to the interior base 25 of screen 20. In such case, the base would comprise a double screen for conducting the current and for providing a stable support.

What I claim is:

1. An electrolytic anode for cells in which chlorine or a radical containing chlorine is formed at the anode comprising a screen housing formed of a passivating metal having a coating thereon comprising a metal of the platinum family on its inner surface, and said housing containing loose electrically conductive corrosion resistant anode material.

2. An electrolytic anode for cells in which chlorine or a radiacal containing chlorine is formed at the anode, said anode comprising titanium in the form of a screen housing for insertion in an electrolyte, a coating of platinum applied to at least the inner surface of said screen, and loose graphite particles arranged in said housing, at least some of which bear against the platinum-coated screen.

3. An electrolytic anode as defined in claim 2 in which opening means leading into said housing are provided through which graphite particles may be introduced into the housing.

4. An electrolytic anode as defined in claim 2 in which the bottom of the housing is in the form of a U-shaped screen arranged within and secured to an outer screen housing.

5. An electrolytic anode for cells in which chlorine or a chlorine containing radical is formed at the anode, said anode comprising titanium in the form of a screen housing for insertion in an electrolyte and a tube composed of a passivating metal extending upwardly from said housing, a coating of platinum applied to at least the inner surface of said screen housing, loose graphite particles arranged in said housing, at least a portion of which bear against the platinum-coated screen and at least some of said particles extending upwarly in said tube which fall into said housing as the anode particles within the housing become partly consumed to thereby provide a substantially constant anode surface.

6. An electrolytic anode as defined in claim 5 in which a stopper is provided to close said tube to prevent loss of chlorine.

7. An electrolytic anode for cells in which chlorine or a chlorine containing radical is formed at the anode com-

prising titanium in the form of a screen housing for insertion in an electrolyte containing a chlorine compound, a tube formed of a passivating metal connected to and extending upwardly from said housing, a coating of platinum applied to at least the inner surface of the screen, loose rounded graphite particles arranged in said housing around which chlorine rises rapidly, some of which particles bear against the platinum coated screen and other contact each other to form an anode surface including the platinum-coated titanium and the surface of each particle within the housing, and at least some of said graphite particles extending upwardly in said tube and being arranged to fall into said housing when particles within the housing become partly consumed to thereby provide a substantially constant anode surface.

8. An electrolytic anode as defined in claim 7 in which the bottom portion of the titanium screen is substantially flat and is coated on both its inner and outer sides with platinum.

9. An electrolytic anode as defined in claim 7 in which the inner and outer surfaces of the titanium screen housing are coated with platinum.

10. An electrolytic anode as defined in claim 7 in which means are provided to internally support the screen housing.

11. An electrolytic anode for cells in which chlorine or a radical containing chlorine is formed at the anode comprising loose graphite particles and means for supporting said particles including a screen housing formed of a passivating metal having a coating thereon comprising a metal of the platinum family on its inner surface, said means further including spaced parallel and spaced longitudinally arranged titanium wires connected to the housing and having a coating of platinum thereon.

References Cited by the Examiner

UNITED STATES PATENTS

1,868,052	7/1932	Dubpernell	204—285
2,865,832	12/1958	Pitzer	204—285
2,944,956	7/1960	Blue et al.	204—285
3,074,858	1/1963	Riding	204—290
3,103,484	9/1963	Messner	204—290

FOREIGN PATENTS

634,495	1/1962	Canada.
845,043	8/1960	Great Britain.

JOHN H. MACK, *Primary Examiner.*

D. R. JORDAN, *Assistant Examiner.*