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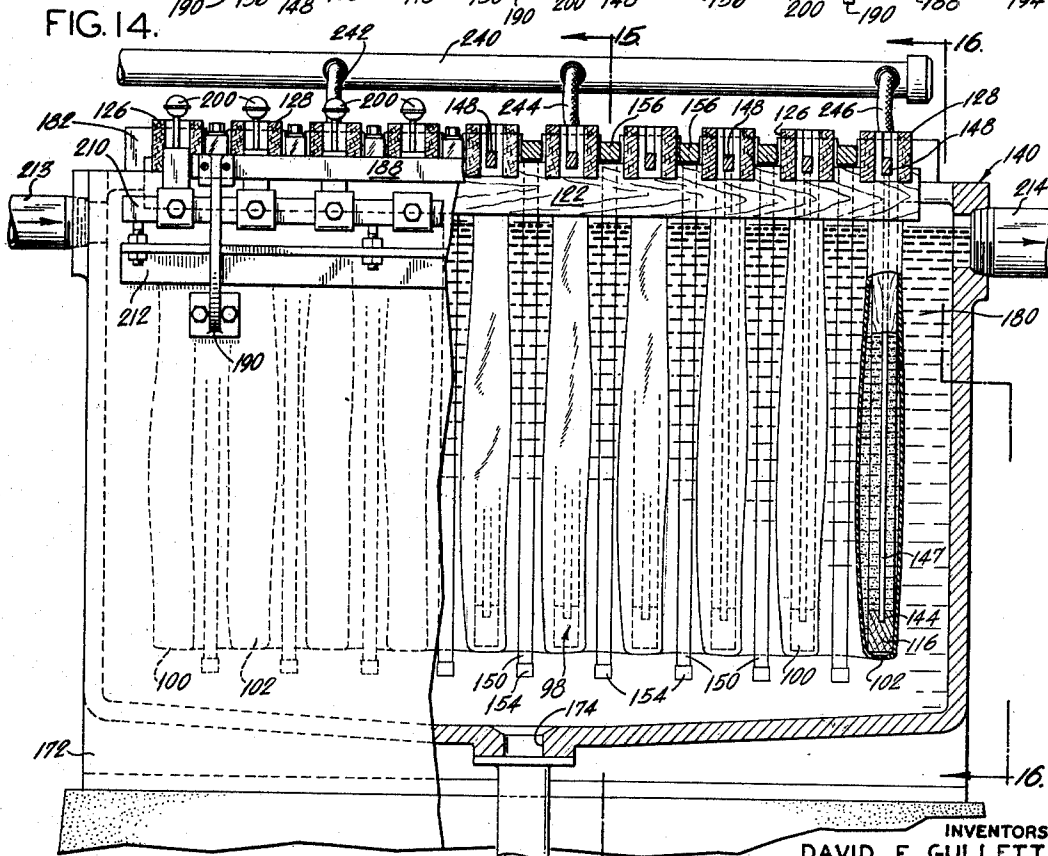
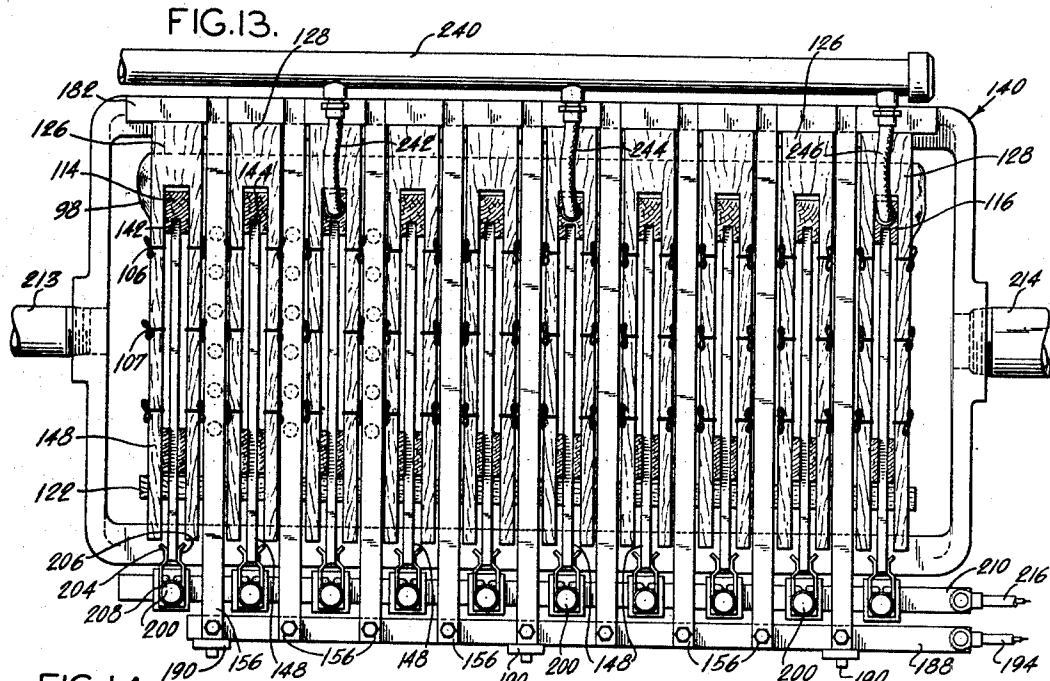
D. E. GULLETT ET AL

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APPARATUS FOR THE ELECTROWINNING OF MANGANESE

Filed March 11, 1966

4 Sheets-Sheet 2



INVENTORS
DAVID E. GULLETT
EDMOND F. REYNOLDS
BY *Howson & Howson*
ATTY IN CHARGE

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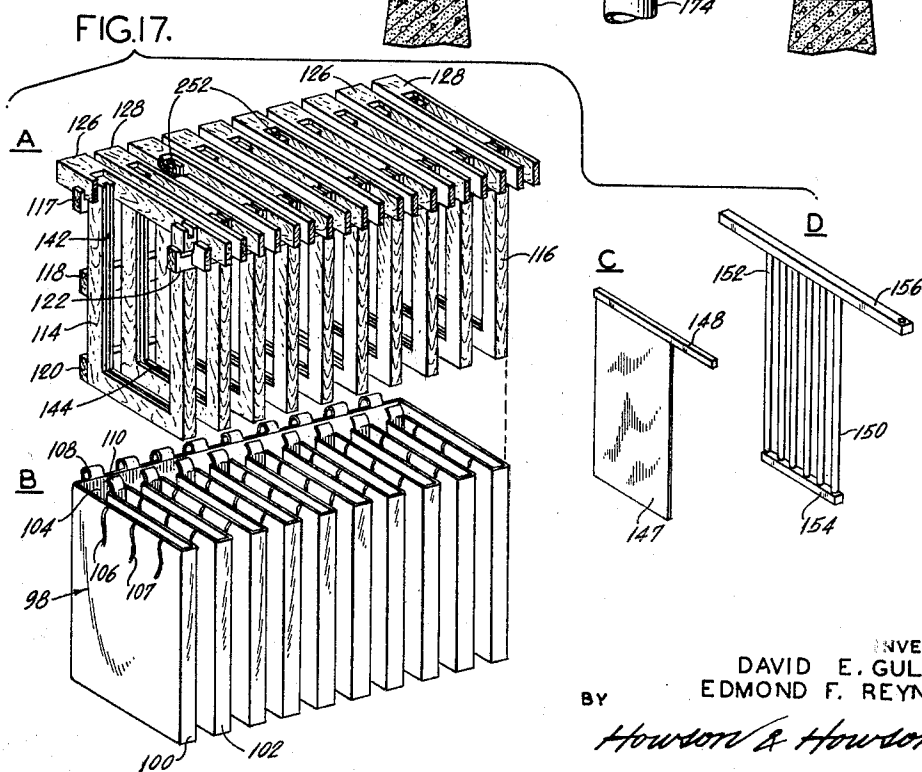
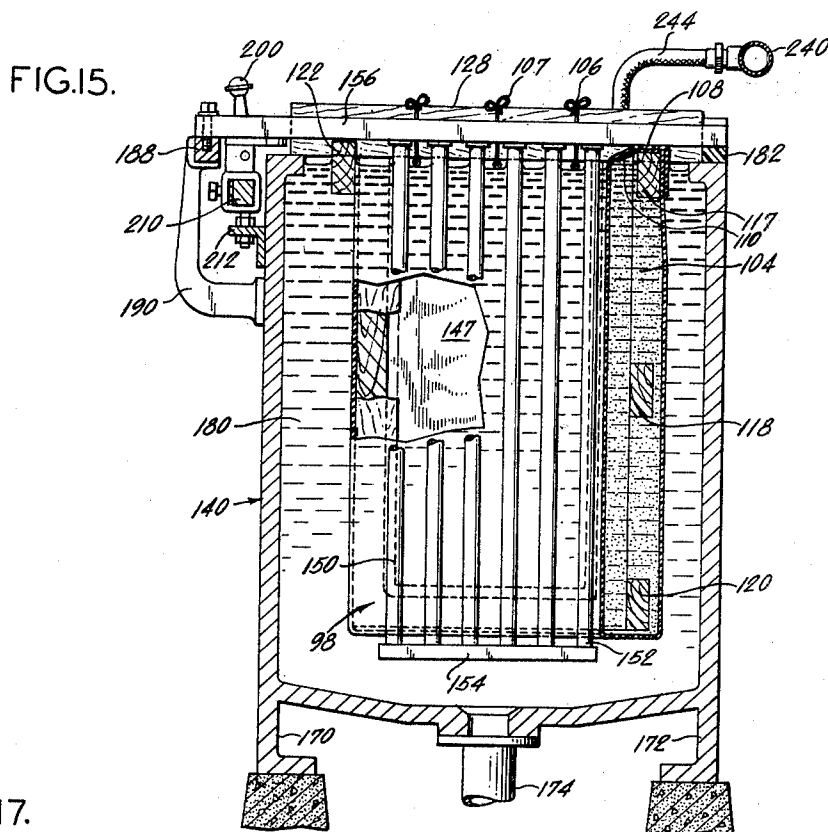
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FIG. 16.

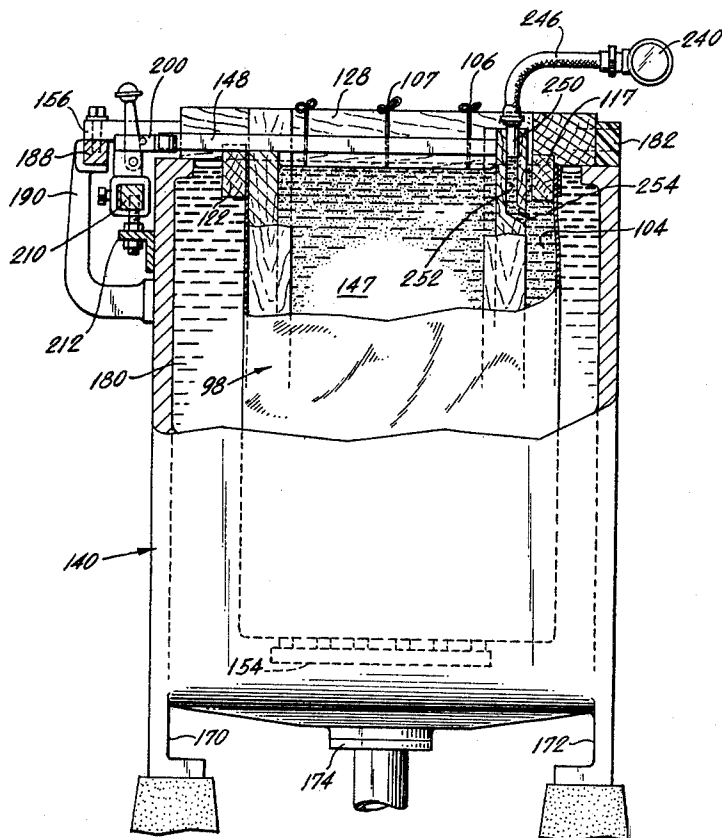
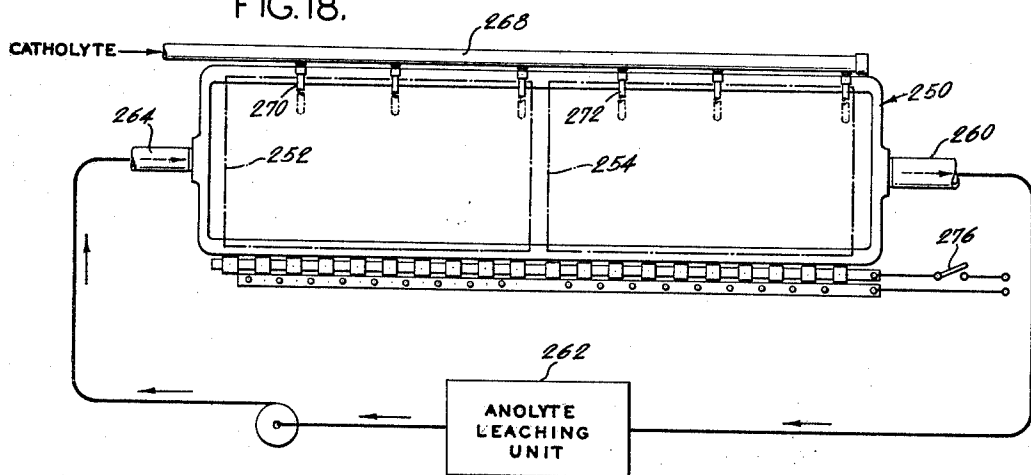


FIG. 18.



INVENTORS:
DAVID E. GULLETT
EDMOND F. REYNOLDS
BY *Howson & Howson*
ATTYS.

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APPARATUS FOR THE ELECTROWINNING
OF MANGANESE

David E. Gullett and Edmond F. Reynolds, Knoxville,
Tenn., assignors to Foote Mineral Company, Exton, Pa.,
a corporation of Pennsylvania

Filed Mar. 11, 1966, Ser. No. 533,664

Int. Cl. B01k 3/10; C22d 1/24; C23b 5/74

U.S. Cl. 204—263

10 Claims

ABSTRACT OF THE DISCLOSURE

Apparatus for the electrowinning of manganese employing a plurality of alternating cathode plates and anode elements in a manganese-plating bath, which apparatus utilizes an electrolyte-perVIOUS diaphragm of woven textile material to form a single catholyte compartment which separates the cathode elements from the anode elements and which is spaced from the cathode elements to permit free circulation of electrolyte inside the catholyte compartment between the major surfaces of the different cathode elements. A supporting frame supports the cathode elements for easy removal by withdrawal through the open top of the diaphragm, and holds the diaphragm away from the major surfaces of each of the cathode elements to permit the desired free circulation of the catholyte electrolyte.

This invention relates to diaphragms for use in electrolytic processes, particularly electrolytic plating, and to apparatus employing such diaphragms. In one specific form, the invention relates particularly to diaphragms and apparatus for use in the electrodeposition of manganese.

In the electroplating art it is known to separate a cathode element from an anode element during plating by means of a porous diaphragm, to supply a suitable catholyte to the side of the diaphragm on which the cathode element is located, and to supply a suitable anolyte to the other side of the diaphragm. The diaphragm serves to maintain the desired optimum electrolytic compositions at the cathode and anode while permitting the necessary ion migration. In commercial cells for the large-scale plating of materials it is common, and usually a practical necessity, to employ a series of mutually-spaced cathode elements with anode elements positioned between them, and in such cases it is known to provide a separate diaphragm around each cathode element and to supply each such individual diaphragm with a separate flow of catholyte by way of appropriate supply tubes extending from a reservoir of catholyte.

However, with such arrangements it has often been found that there is a very substantial difference between the plating actions produced in the various individual diaphragms. Thus even though some of the cathode elements may be plated in an optimum manner, other cathode elements in the same commercial cell will commonly exhibit poor plating efficiency and poor quality of plating, and excessive formation of byproducts may occur which tends to plug up the diaphragms and in some cases to contaminate the cathode elements themselves. These undesired effects arise primarily because of lack of uniformity in the temperatures and compositions of the catholytes inside the various diaphragms.

Referring particularly to the type of process with specific reference to which the invention will be described in detail, it is known to produce manganese by depositing it electrolytically on a series of cathode plates immersed in an electrolyte, using anode elements which are situated between the cathode plates. This geometric arrangement of interdigitated cathode plates and anode elements has been found commercially desirable in obtaining high ef-

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iciency, high quality plating. However, when each cathode plate is surrounded with an individual diaphragm to form a separate cathode compartment separately supplied with catholyte, we have found that unavoidable differences in temperature and manganese concentration in the catholytes inside the several cathode compartments generally cause inferior plating in at least some of the cells even though it may be satisfactory in others. More particularly, while the proper average manganese concentration can often be provided in the catholyte supply which is distributed to the various cathode compartments, departures from this optimum manganese concentration generally occur in various of the individual cathode compartments; this generally reduces directly the plating efficiency in such compartments and also increases the rate of formation of undesired solid byproducts commonly known as "pink salts" which tend to plug the diaphragm, change the effective resistance of the individual plating cell, and thereby also reduce plating efficiency. Where such "pink salts" are formed in large quantities, they may in fact directly contaminate the cathode plates. Again, while average temperature of the catholyte supplied to the various catholyte compartments can generally be held near the optimum value, individual variations in the temperature in the various cathode compartments commonly occur and result in inferior plating, including so-called "tree" formation and in some cases in the excessive formation and deposition of undesired solids.

Accordingly it is an object of our invention to provide new and useful apparatus for use in electrolytic processes.

Another object is to provide new and useful apparatus for the electrodeposition of materials, such as manganese, upon plural cathode elements.

Another object is to provide new and useful apparatus for electrolytically depositing a material upon plural cathode elements between which are located a plurality of anode elements.

Another object is to provide such apparatus which provides more uniform conditions in the vicinity of the several cathode elements and hence more uniform, and superior, electroplating upon these cathode elements.

A further object is to provide a new and useful diaphragm arrangement for use in electrolytic processes.

Another object is to provide such a diaphragm which enhances the uniformity of conditions in the electrolyte around the several cathode elements and thus improves the quality and efficiency of electroplating.

A further object is to provide new and useful diaphragm arrangements for use in the electrodeposition of manganese.

These and other objects of the invention are achieved by the provision of a novel form of diaphragm and a novel form of apparatus for using it in electrolytic processes. More particularly, in accordance with the invention there is provided a diaphragm shaped to envelop a plurality of cathode elements in a common cathode compartment formed by the diaphragm, while separating the cathode elements from anode elements which are located in the space between the successive cathode elements. The diaphragm is shaped to permit circulation of catholyte between the various cathode elements through the common cathode compartments. In one preferred form the diaphragm comprises a plurality of pockets, each enveloping a different one of the cathode elements, one side of each pocket being open and communicating with a common chamber in the diaphragm which permits circulation of catholyte between the various pockets. A flow of catholyte into the common cathode compartment and a flow of anolyte through the anode compartment is provided. In another form of the diaphragm, the pockets of the above-described diaphragm are open at both ends rather than at one end only so as to comprise, in effect,

a plurality of sleeves extending on opposite sides of one of the cathode elements and each communicating at its opposite open ends with a pair of common chambers within the diaphragm, the two common chambers serving to interconnect the openings in the several sleeves. In still another form the invention may utilize for the diaphragm a continuous, sinuous, tubular sheath following a path which passes back and forth through the array of anode and cathode elements and enveloping all of the cathode elements in sequence on their opposite sides; a flow of catholyte is then supplied to the interior of the sheath so that a circulation of catholyte occurs between the various cathode elements.

Utilizing such diaphragm arrangements in which the cathode elements are enclosed in a common catholyte compartment by a single diaphragm, it has been found that superior results are obtained, apparently due to the greater uniformity of the composition and temperature of the catholyte adjacent the various cathode elements, which in turn is apparently due to the mixing and circulating of the catholyte in the common cathode compartment. In the specific case of the electroplating of manganese, this has resulted in a greater uniformity of high-quality, high-efficiency plating on the various cathode elements and a reduction in the rate of formation of undesired byproducts such as "pink salts."

Other objects and features of the invention will be more fully understood from a consideration of the following detailed description, taken in connection with the accompanying drawings, in which:

FIGURES 1, 2, 3 and 4 are, respectively, top, front elevation, end elevation and fragmentary perspective views of one preferred form of diaphragm arrangement in accordance with the invention, showing also preferred locations of the anode and cathode elements with respect to the diaphragm;

FIGURES 5, 6, 7 and 8 are, respectively, top, front elevation, end elevation and fragmentary perspective views of another diaphragm arrangement in accordance with the invention, showing also a preferred location of the anode and cathode elements with respect to the diaphragm;

FIGURES 9, 10, 11 and 12 are, respectively, top, front elevation, end elevation and fragmentary perspective views of a third diaphragm arrangement in accordance with the invention, showing also a preferred location of the anode and cathode elements with respect to the diaphragm;

FIGURE 13 is a top view of electroplating apparatus in accordance with a preferred embodiment of the invention, including structures for supporting the diaphragm and for supplying appropriate catholyte, anolyte and electrical current flow;

FIGURE 14 is a front view of the apparatus shown in FIGURE 13, with parts broken away;

FIGURE 15 is a sectional view, taken along lines 15—15 of FIGURE 14, with parts broken away;

FIGURE 16 is a sectional view, taken along lines 16—16 of FIGURE 14;

FIGURE 17 is a perspective view showing at A, B, C and D thereof various parts of the embodiment of FIGURE 14 separated from each other for clarity of exposition; and

FIGURE 18 is a schematic view illustrating a system employing a plurality of common-cathode compartment cells such as are shown in FIGURE 14.

Referring now to the diaphragm arrangement shown particularly clearly in FIGURES 1—4, the diaphragm 10 may be made of any of a number of different materials previously used in diaphragms for electrolytic processes. The material used is ordinarily selected to provide the proper permeability and electrical resistance, to be chemically resistant to the electrolyte utilized, and to be of good mechanical strength. It is preferred to use for this purpose textile materials, such as the material known by the trade name Dynel, which has previously been used in

other forms of diaphragms and is a copolymer of vinyl chloride and acrylonitrile.

The diaphragm 10 comprises a plurality of pockets such as 12, 14 and 16 of rectangular cross-section which are open at the top and are also open at their respective rearward sides such as 18, 20 and 22. The open sides of the individual pockets open into, and freely communicate with, a common chamber portion 26 of the diaphragm 10 which extends the full length of the assembly of pockets and also the full height of each pocket. Such a diaphragm may be made by cutting appropriately shaped-pieces of diaphragm material and sewing them together, with appropriate cementing along the seams if desired, in the manner which will be apparent to one skilled in the art. Preferably the seams are sewed externally and then the entire diaphragm turned inside out. Also preferably provided (see FIG. 4) are tapes such as 30, 31, 32, 33, 34 and 35 and tie strings such as 38, 40 and 42 for attaching the diaphragm to a supporting frame to be described hereinafter.

The cathode elements such as 44 and 46, each of which may comprise an electrically-conductive rectangular plate, are suspended in the pockets such as 12, 14, one plate to each pocket. Between the diaphragm pockets are suspended the anode elements such as 50, 52, for example, one anode element between each pair of pockets, each anode element typically comprising a group of vertically-disposed electrically-conductive rods. The manner of mounting of the cathode plates and the anode rods will be particularly described with respect to other figures of the drawings.

When in use, the interior of the diaphragm 10 is supplied with a suitable catholyte, and the diaphragm therefore comprises a common catholyte compartment for all of the cathode elements. The diaphragm is open at the top as is usual in electrolytic diaphragms, but is elsewhere closed so as to separate all of the cathode elements from all of the anode elements. It will be appreciated that this common catholyte compartment diaphragm in which the individual cathode pockets communicate with a common chamber 26 permits the desired circulation and uniform mixing of the catholyte which has been found to produce a substantially uniform temperature and composition of electrolyte around all of the cathode elements, with resultant improvement in plating quality and efficiency and with a reduction in generation of undesired solid byproducts.

The alternative form of diaphragm 58 shown in FIGURES 5—8 is similar to that shown in FIGURES 1—4, with the exception that in diaphragm 58 there is a common chamber along the front as well as along the back of the diaphragm and the individual cathode "pockets" are open at both ends to two common chambers. More particularly, in this embodiment the cathode elements such as 44, 46 are enveloped on their opposite major faces by sleeve regions such as 60, 62 of diaphragm 58, which communicate along their front vertical edges such as 64, 66 and along their rear vertical edges such as 67 and 68 with common chambers 70 and 72, respectively. The latter common chambers extend along the full length and height of the diaphragm 58. Appropriate tabs and strings are preferably provided for support, as in the embodiment previously described. In this case the anode elements, such as 50, 52 are again placed directly between successive cathode plates, but in this case are surrounded on all four sides by the diaphragm 58. A single common catholyte compartment is thereby again provided, which communicates with the regions around each of the cathode plates so that the temperatures and compositions of the catholyte at the various cathode plates are substantially the same. However, in the present embodiment the surrounding of the anode elements on all four sides by the diaphragm 58 tends to reduce somewhat the free circulation of the anolyte to the various anode elements,

and for this reason the diaphragm arrangement of FIGURES 1-4 is preferred for many applications.

FIGURES 9-12 illustrate a third diaphragm arrangement in accordance with the invention. In this case the diaphragm 76 comprises a single, continuous, sinuous tubular sheath of rectangular cross-section which follows a path oscillating back and forth through the array of cathode and anode elements, enveloping the successive cathode elements such as 44, 46 in sequence, separating them from the anode elements and completely enclosing them except at the top, which is left open. In this arrangement the catholyte may be introduced into the rear-most portions of the diaphragm from the top. Again, the diaphragm arrangement is such that circulation and intermixing of the catholyte reaching the cathode elements is provided, with resultant improvement in uniformity of the temperature and composition of the catholyte at the various cathode elements and consequent improvement in quality and efficiency of plating and reduction in generation of undesired solid byproducts.

There will now be described with particular reference to FIGURES 13-17 one specific form of apparatus suitable for the electrodeposition of manganese utilizing the preferred form of diaphragm shown in FIGURES 1-4, it being understood however that the various expedients described with reference to this specific form of the invention may readily be adapted to supporting and supplying of electrolyte and electric current to other forms of diaphragm in accordance with the invention, such as the two forms illustrated in FIGURES 8 and 12.

The basic arrangement of the apparatus utilizing this particular form of the invention is readily understood from a consideration of FIGURE 17. The diaphragm used, shown at B of FIGURE 17, is of the type also illustrated in FIGURE 4 and in this example utilizes ten pockets such as 100, 102 closed at the front, bottom and sides but open at the top, the rear edge of each pocket communicating with the common chamber 104 near the rear of the diaphragm 98. The diaphragm is made of a textile fabric of the above-mentioned Dynel, by cutting appropriately sized pieces, sewing them together at the edges, turning the resultant diaphragm inside out and, if desired, sealing the sewn edges with a suitable compound. Appropriate ties such as 106, 107 are provided, and may be of the synthetic material known by the trade name Teflon, which material may also be used for the thread with which the diaphragm is sewn together. The tapes such as 108, 110 may be integral parts of the diaphragm, left during the cutting out of the pieces of the diaphragm, or may be sewn to the diaphragm.

The diaphragm shown at B of FIGURE 17 is pulled up onto and around a preformed wooden support structure shown at A of FIGURE 17. The support frame comprises a plurality of individual generally U-shaped frame members such as 114 and 116, in this case ten, one for each of the pockets in the diaphragm. The individual support frames are held together in parallel spaced relationship by means of three longitudinal members 117, 118 and 120, at the rear of the assembly and by one longitudinal member 122 at the front of the assembly, which is secured to the undersides of the cross members such as 126 and 128 which extend transversely across the top of the assembly and are secured to the individual support frames. When the diaphragm 98 is pulled up into position, each pocket thereof such as 100, 102 envelopes a different of the U-shaped support frames, and the rear of the diaphragm passes behind the longitudinal support members 117, 118 and 120 and just behind the front longitudinal member 122. When so positioned, the diaphragm is secured by tying the ties such as 106, 107 around the cross members such as 126, 128 and by passing the tapes such as 108, 110 over the top longitudinal member 117 from opposite sides and securing them together or to the frame in any convenient manner, as is shown in FIGURES 13-16 and especially in FIGURE 15. The cross

members such as 126, 128 extend rearwardly and forwardly of the assembly to provide overhanging arms by means of which the assembly may be supported on the opposite edges of an electrolyte tank 140 shown in FIGURES 13-16.

Each of the U-shaped support frames is provided with a corresponding U-shaped slot such as 142, 144 in the interior faces thereof, and into each such slot is slid a conductive metal cathode plate of rectangular form such as is shown at C of FIGURE 17, the plate being secured at its upper edge to a conductive support bar 148. The spaces between the successive cross members such as 126, 128 and the spaces between the pockets in the diaphragm 98 are occupied by anode assemblies such as that shown at D of FIGURE 17, comprising in each case a set of vertically-disposed parallel conductive rods such as 150, 152 secured together at the bottom by a cross bar 154 and at the top by a conductive cross bar 156 which extends rearwardly and forwardly of the array of rods so that it may be also supported by the opposite edges of the electrolyte tank 140.

FIGURES 13-16 show the complete assembly in position for use in electroplating of manganese, and illustrate further preferred details of construction not shown in FIGURE 17. Referring particularly to FIGURES 13-16, the electrolyte-containing tank 140 is generally rectangular in form and may be provided with mounting feet 170, 172 and a suitable drain arrangement 174 at the bottom thereof. It is made of a chemically inert material, which in some cases may also be an electrical insulator but in the present example is assumed to be lead, which is an electrical conductor. The support frame assembly, which may be made of pieces of wood secured together by screws and/or by glue, depends from the opposite top edges of the tank so that the diaphragm 98, the cathode plates such as 147 and the anode rods such as 150 hang down into the electrolyte 180. The rearward ends of the anode top cross bars such as 156 (see FIGURE 15) rest on the top of an electrically insulating strip 182 on the top rear edge of the electrolyte tank. The front ends of the anode top cross bars lie on top of, and are bolted to, an anode supply bus bar 188 which extends along the front of the tank 140 near the top thereof and is supported from the tank by means of insulating support arms such as 190. An appropriate conductive anode voltage supply line 194 (FIGURE 13) is connected to the right-hand extreme of the anode bus bar 188, through which the plating current is supplied from an appropriate electrical source.

Each of the cathode support bars such as 148 extends forwardly to the front edge of the tank 140 to be contacted by a releasable electrical contactor such as 200. Because the cathode plates are normally removed and replaced much more often than the bolted-on anode assemblies, the cathode contactors are preferably of a type which may easily be manipulated alternatively to release the cathode plate or to grasp it firmly to provide good electrical contact. Any of a large variety of arrangements may be utilized for this purpose, and in the present example there is shown an arrangement in which each plate is grasped on opposite sides by means of fingers such as 204, 206 when the connector control knob 208 is in the position shown, the contactors being spread to release the cathode plate when the knob 208 is rotated toward the interior of the tank. Each such contactor assembly 200 is mounted in good electrical contact with a cathode supply bus bar 210 which extends along the length of the tank near the upper edge thereof and which is supported from the tank by appropriate electrically insulating support structures such as 212. The extreme right-hand end of cathode bus bar as shown in FIGURE 13 is connected to a suitable cathode supply voltage cable 216 which is maintained negative and supplied with the necessary plating current from the above-mentioned appropriate electrical source.

A suitable anolyte solution is supplied to the interior of the tank by way of an appropriate anolyte input line 213 located near the top and center of the left-hand end of tank 140 as shown in FIGURES 13 and 14. The anolyte flows through the tank, leaving the tank by way of the outlet line 214 connected near the top and center of the opposite end of tank 140. The latter outlet line serves as an overflow outlet to maintain the top level of the electrolyte at the desired height.

An appropriate catholyte is supplied from a catholyte source by way of a tube 240 and several catholyte branch supply lines 242, 244 and 246 which feed electrolyte from tube 240 into the common chamber 104 at the rear of diaphragm 98. The exact number of such branch supply lines for the catholyte is not critical, although it is preferred to use at least several of them. As can be seen particularly clearly in FIGURES 13 and 16, each of the catholyte supply branch lines such as 246, which may be of flexible inert tubing, is connected to the top of a tube such as 250 which extends upward from, and is tightly held in, a channel 252 in one of the rearward upwardly extending members of one of the U-shaped support frames. The channel 252 opens out rearwardly into the common chamber 104, as shown at 254 of FIGURE 16, so that the catholyte is thereby supplied to the latter common chamber.

The catholyte supplied to the common catholyte compartment fills the diaphragm completely, and generally seeps slowly through the walls of the diaphragm and to some extent over the top of the diaphragm to slowly mix with the anolyte solution, which is constantly being replenished by the anolyte flow. As shown, the pockets of the diaphragm 98 not only fit rather loosely over the corresponding U-shaped support frame but are also spaced from the cathode plates due to the thickness of the U-shaped frames, so as to permit circulation, intermixing and interchange of catholyte among the various cathode elements and adequate circulation within each diaphragm pocket.

The arrangement shown in FIGURES 13-17 is particularly adapted for the commercial recovery of manganese by electroplating. Accordingly, in ordinary use a set of cathode plates are placed into the assembly, the catholyte and anolyte supplies turned on, the plating current applied, and plating continued until the desired coating of the plates with manganese has occurred. The plates are then removed and the manganese plating removed from the plates, after which the same or other cathode plates are inserted again into the plating apparatus and the process repeated. When this process has been repeated a relatively large number of times, some accumulation of undesired solid products in the pores and at the bottom of the diaphragm may occur, and the diaphragm may then be cleaned out by flushing with an appropriate cleaning solution while remaining mounted in the tank, with the cathode and anode elements preferably removed; or, the diaphragm may be removed from the support, cleaned separately, and replaced on the frame for reuse, which can be done a number of times.

FIGURE 18 illustrates schematically that, while for convenience the drawings thus far discussed have shown systems employing but a single common catholyte compartment, a number of such arrangements may be operated side by side in the same tank from the same electrical current source. Thus FIGURE 18 shows an elongated electrolyte tank 250 having two identical plating assemblies 252 and 254 therein, each comprising a common-cathode-compartment diaphragm with supporting frame and cathode and anode elements as described with reference to FIGURES 13-17. Also shown in FIGURE 18 is an arrangement by which the anolyte from the outlet line 260 is recirculated through an anolyte leaching unit 262 and pumped back to the anolyte input line 264 to be reused. The same catholyte supply pipe 268

supplies the catholyte to the two units by way of appropriate branch lines such as 270 and 272 for example. A common electrical supply arrangement for the two units is also shown, operated by a control switch 276.

Similarly, by techniques which will readily occur to one skilled in the art, the alternative forms of diaphragm structures illustrated in FIGURES 8 and 12 may be suitably mounted in an electrolyte tank, with appropriate cathode and anode elements, and supplied with appropriate anolyte and catholyte solutions and plating currents so as to operate in the manner described above with reference to FIGURES 13-18.

It will be understood that while the material Dynel is preferred for use in the diaphragm of the invention, other known diaphragm materials such as woven filaments of Orlon, or textile materials of cotton or the like, may be utilized instead where appropriate to the particular use.

Without thereby in any way limiting the scope of the invention, the following specific example of a plating process utilizing the arrangement of apparatus particularly illustrated in FIGURES 13-17 will now be given.

The plating assembly may be like that illustrated in FIGURE 18, using two ten-plate units each of the type shown in FIGURES 13 and 14. The 20 rectangular cathode plates may each be 34" x 20" in size, the catholyte fed to the interior of the diaphragm may comprise a conventional manganese sulphate plating solution containing 32 grams/liter of manganese and 125 grams/liter of ammonium sulphate, minor amounts of other sulphates also being added in some cases as is known in the art. A typical pH for the feed catholyte is 7.3, and it may be fed to the diaphragm at 35° C. and at a flow rate of one gallon/minute. The anolyte may be a manganese sulphate solution comprising 16 grams/liter of manganese and 135 grams/liter of ammonium sulphate, the solution having a pH of 1.0, a flow rate of eight gals./minute, an entering temperature of 35° C. and an exiting temperature of 43° C.

In this case the catholyte in the diaphragm during operation will typically comprise 15 grams/liter of manganese and 125 grams/liter of ammonium sulphate, with a pH of about 8.7 and a temperature of about 45° C. Whereas in previously-known forms of diaphragm the catholyte in the diaphragm during use in such a case would typically exhibit temperature variations of about $\pm 2^\circ$ C. and manganese variations of about ± 5 grams/liter, in the previously-described form of the invention the temperature variations in the catholyte in the diaphragm are only $\pm 0.1^\circ$ C. and the manganese variations only about ± 0.5 gram/liter, with resultant improvement in plating quality and efficiency and with increased longevity of the diaphragm due to slower formation of undesired solid byproducts.

Typical plating currents in this example are around 6700 amperes, or 45 amperes per square foot of plated cathode surface. Plating may typically be continued for 16 to 32 hours, and the cathode plates replaced, and this operation repeated at least 20 times before the diaphragm requires cleaning by known procedures.

The two diaphragms used in this example, each containing 10 cathode plates, may each be about 44" in length, about 36" in height and about 21" in depth front-to-back with 2"-wide pockets and 2.5" wide spaces between pockets. The common chamber may be about 1" in front-to-back depth.

While the invention has been described with particular reference to specific embodiments thereof in the interest of complete definiteness, it may be embodied in any of a variety of forms differing from those specifically described, without departing from the scope and spirit of the invention as defined by the appended claims.

We claim:

1. In apparatus for the electroplating of manganese comprising a container for electrolyte, a plurality of spaced cathode plates disposed in said container so as to be bathed

by electrolyte in said container, a plurality of anode elements disposed between and spaced from said plates, means for applying to said anode elements an electrical potential positive with respect to said cathode plates, electrolyte-pervious diaphragm means separating said cathode plates from said anode elements, means for supplying a flow of catholyte into said container on the cathode side of said diaphragm, and means for supplying a flow of anolyte into and out of said container on the anode side of said diaphragm, the improvement according to which said diaphragm means comprises a diaphragm separating said cathode plates from said anode elements and closed on its sides and bottom to form a common catholyte compartment enveloping said cathode plates, said diaphragm being spaced from the major faces of said plates to provide for unimpeded circulation of said catholyte to said plates and over both major faces thereof.

2. Apparatus in accordance with claim 1, in which said diaphragm defines a common catholyte compartment comprising a plurality of individual catholyte chambers each enveloping a different one of said cathode plates and a common catholyte chamber of a volume large compared with the volume of each of said individual catholyte chambers and freely communicating with each of said individual catholyte chambers.

3. Apparatus in accordance with claim 1, in which said diaphragm is open at its top to permit insertion and withdrawal of cathode plates into said diaphragm from the top of said apparatus.

4. In the apparatus of claim 1, means supporting said diaphragm so as to hold it spaced from said major faces of said cathode plates.

5. Apparatus in accordance with claim 4, in which said supporting means comprises a rigid frame in said container.

6. Apparatus for the electroplating of manganese, comprising:

- a container for a manganese-plating electrolyte;
- a supporting frame in said container;
- a plurality of vertical, parallel, spaced-apart cathode plates removably mounted in a row on said frame and within said container, with their bottom ends spaced above the bottom of said container;
- a plurality of anode elements disposed between said cathode plates;
- means for applying to said anode elements a positive potential with respect to said cathode plates;
- a continuous open-topped electrolyte-pervious diaphragm separating said cathode plates from said anode elements, enveloping the sides and bottom of each of said cathode plates, and enclosing all of said cathode plates in a common catholyte compartment;
- means for providing a flow of catholyte into said catholyte compartments;
- said frame supporting said diaphragm and holding it

spaced from both major surfaces of each of said cathode plates thereby to provide for free circulation of said catholyte to said major surfaces of said plates; and

means for providing a flow of anolyte into and out of said container exterior of said common catholyte compartment.

7. Apparatus in accordance with claim 6, in which said common catholyte compartment comprises a plurality of pockets each enveloping the bottom and three sides of one of said cathode plates, and a common chamber communicating with said pockets at their fourth sides.

8. Apparatus in accordance with claim 7, in which said frame comprises a plurality of individual support frames, one for each of said cathode plates, each of said support frames being adapted to support its corresponding cathode plate for upward withdrawal thereof from said container and to hold said diaphragm away from both major surfaces of said corresponding cathode plate, said diaphragm being configured to fit loosely around the sides and bottom of each of said support frames and to be secured thereto.

9. Electroplating apparatus, comprising:

- a plurality of cathode elements;
- at least one anode element spaced from and between different ones of said cathode elements;
- a porous diaphragm enveloping said cathode elements and separating each of them from said anode element, said diaphragm being sufficiently spaced from said cathode elements to provide communication internally thereof between each of said cathode elements, whereby electrolyte within said diaphragm can circulate freely between different ones of said cathode elements but is restrained from circulating to said anode element.

10. The apparatus of claim 9, in which said diaphragm is of a textile fabric, and comprising support means for holding said diaphragm in said spaced position.

References Cited

UNITED STATES PATENTS

1,815,078	7/1931	Smith	204—253
2,361,974	11/1944	Smith	204—260
2,944,956	7/1960	Blue et al.	204—296 XR
3,337,443	8/1967	Raetzsch et al.	204—258 XR

FOREIGN PATENTS

375,085	5/1923	Germany.
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JOHN H. MACK, Primary Examiner

D. R. JORDAN, Assistant Examiner

U.S. Cl. X.R.

204—105, 257