Nov. 8, 1955 A. R. GODSEY, JR 2,723,230

ANODE FOR ELECTROWINNING OF MANGANESE

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Fig. 1

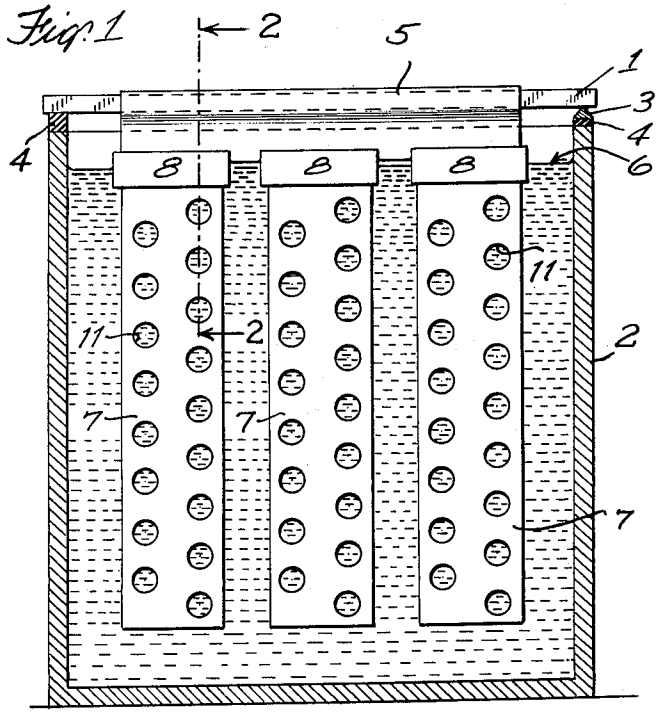
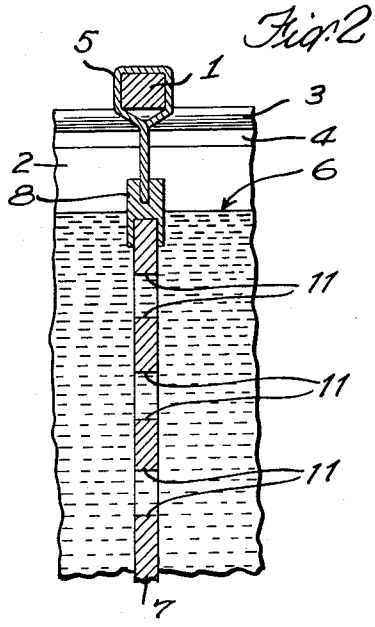


Fig. 2



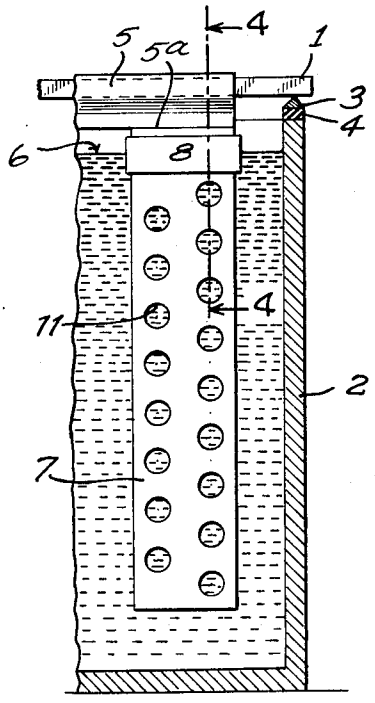


Fig. 3

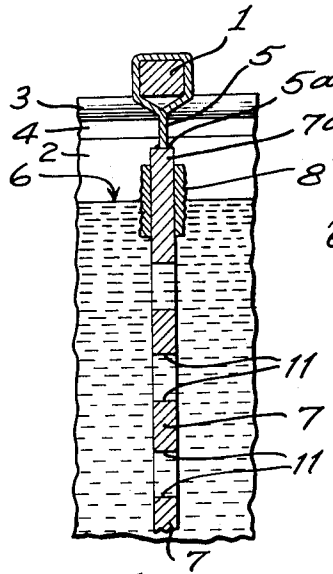
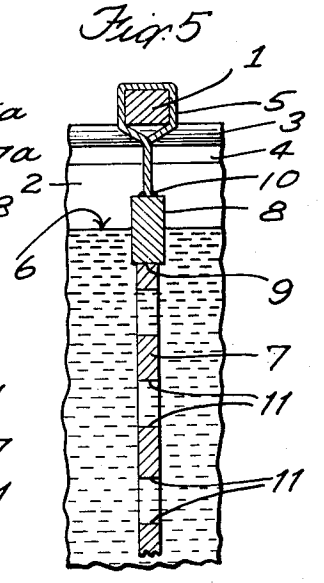


Fig. 4

Fig. 5



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ANODE FOR ELECTROWINNING OF MANGANESE

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Application January 21, 1953, Serial No. 332,428

3 Claims. (Cl. 204—286)

This invention relates to the electrowinning of manganese, more especially to the anodes used in the cells of which metallic manganese is cathodically deposited from manganese containing solutions.

In that art important problems arise in connection with the anodes and their effects. With anodes of lead, used in other electrowinning processes for their resistance to corrosion 50% of the manganese in solution may be precipitated at the anode as manganese dioxide, an undesirable product. This was shown by Shelton and Royer in Transactions of the American Electrochemical Society, vol. 74, pp. 447–458 (1938).

There are a number of patents and publications relating to the reduction of the formation of manganese dioxide by the use of anodes having special compositions. Thus, Fink and Kolodney, in U. S. Patent 2,320,773, proposed an anode of 1–15% antimony, 9–50% tin and a small but effective amount to about 4.4% cobalt with the balance lead. With anodes of this type surface layers of mixed oxides are formed which minimize the formation of manganese dioxide.

Mantell, in U. S. Patent 2,340,400, found that the Fink and Kolodney anodes, while minimizing the formation of manganese dioxide were subject to corrosion and loss of constituents, as well as impairment of the catholytic coating during loss of constituents, with increased production of manganese dioxide when the coatings were ruptured. Mantell specified an anode with better corrosion resistance and longer life in service having a composition of 0.02 to 0.04% cobalt, 20 to 25% tin, 4 to 6% antimony, with balance lead including such silver as is normally associated with the lead.

Tainton, in U. S. Patent 1,759,493, proposed for zinc electrowinning an insoluble anode of lead containing 1% silver, as well as one containing 1% silver and 1 to 5% arsenic.

Hanley and Jacobs, in U. S. Patent 2,439,805, proposed an alloy containing 1 to 3% silver, balance lead as an anode for manganese electrowinning under specific conditions to keep the losses of manganese as manganese dioxide at the anode at a low level.

The electrolyte commercially used is essentially a manganous sulfate-ammonium sulfate solution separated by porous diaphragms into anolyte portions and catholyte portions. The former are distinctly acid due to the presence of sulfuric acid and the latter are distinctly alkaline due to the presence of ammonia. The following data is typical of anolyte and catholyte compositions:

	Catholyte	Anolyte
pH	7 to 9	0.8 to 1.4.
Grams per liter of Mn (as $MnSO_4$)	12 to 16	12 to 16.
Grams per liter of $(NH_4)_2SO_4$	120 to 200	120 to 200.

Anodes for continuous large scale production of manganese by electrowinning processes must not only act with low loss of manganese as manganese dioxide, but must also be resistant to attack by the anolyte solution in contact with the anode surfaces, must be suitable structurally or be readily repairable by operations such as welding or lead burning and must have long life.

For short cycles of several hours or days or even a month or so, alloys of 1% silver, 1% arsenic, balance lead appear to have reasonably satisfactory qualities. In present day commercial operation, the cell and anodes are cleaned periodically every 7 to 8 weeks. Tests in which the anodes were weighed and examined at the beginning and end of each cleaning cycle (anode cleaning involved removal of loose MnO_2 scales from submerged areas and crystallized salts from the unsubmerged areas) have shown that for a period of 5 cleaning cycles, or 35 to 38 weeks, the 1% silver, 1% arsenic, balance lead alloy showed little corrosion and met the other anode requirements. During this period no appreciable weight loss was noted nor any serious deterioration. Furthermore, average cell voltage of 1% silver, 1% arsenic, balance lead anodes was about 0.1 volt lower than average cell voltage of 1% silver balance lead anodes. However, after the initial operating period of about 35 weeks, 1% silver, 1% arsenic, balance lead anodes deteriorated rapidly and at the end of 51 weeks the anodes were at the end of their useful life. A second test cell using 1% silver, 1% arsenic, balance lead anodes gave an even shorter useful life of 39 weeks.

Deterioration of the 1% silver, 1% arsenic, balance lead alloy occurred in all submerged areas. The alloy became hard and brittle, pieces and even large sections sometimes fell off in the cell. At the cross section of the break the alloy appeared to have become somewhat crystalline in structure except for a possible thin core of metal. Repairs were very difficult if not impossible as lead burners could not burn to anything but the thin metal core which in most cases did not have sufficient strength and thickness to support the burn. This sudden deterioration of the 1% silver, 1% arsenic, balance lead alloy and the inability to make repairs eliminated serious consideration of the alloy as a commercial anode for manganese electrowinning.

The Tainton anode of 1% silver balance lead alloy was found in commercial operation to have poor operating characteristics in that it was badly corroded at the solution line. In plant operation in order to use them at all, the 1% silver balance lead anodes must be removed from the cells after every two or three cell cleaning cycles, that is 14 to 21 weeks, and be repaired to eliminate the damage at the solution line and the danger of the anode falling into the cell by extreme reduction of cross sectional area at the solution line. Repair did not eliminate corrosion but did permit continued use of the anode until solution line corrosion recurred at the end of another 14–21 week period. Without repair, corrosion at the solution line would ultimately cause failure of the anode, with all or most of the anode dropping into the solution at the end of approximately 40 weeks.

Alloys of silver content from 0.1% to 1% balance lead were tested for soundness, i. e., freedom from shrinkage cracks, blow holes, etc. Those containing 0.75% silver or less showed shrinkage cracks on casting, particularly where perforated sheets or strips were cast, a preferred anode form. Alloys composed of 0.75 to 0.95% silver balance lead were sounder than those containing higher or lower amounts of silver but suffered from the disadvantage of corrosion at the solution line.

In the silver 1% balance lead anode the rate of corrosion of the main body in contact with the electrolyte is at a rate of over 1/32" reduction in thickness per year while corrosion at the solution line or the electrolyte-air interface is at a rate of 7/16" reduction in thickness per year or 14 times that of the underwater corrosion.

Underwater corrosion, i. e. at all portions below the

solution line portion, with attendant weight loss and reduction of anode thickness takes place at a much lower rate than corrosion at the solution line portion in the case of the 1% silver balance lead anode. In typical cases the anodes are originally 5/16" thick and when they are corroded to approximately 3/16" or less in thickness they have lost enough physical strength so that they must be discarded. Underwater corrosion is at such a rate that anode lives of about 150 weeks are estimated if corrosion at the solution line portion were at about the same rate as at the portions below the solution line portion. It has been found that if the water line corrosion at the end of 14 to 21 weeks is corrected by repair in which new silver lead alloy is added to replace that corroded away at the solution line, approximately seven repairs may be made as are necessary before the limiting factor of underwater corrosion and its resultant reduction in anode thickness with loss of strength is the controlling variable. At this time, approximately 140–150 weeks, the anode is corroded at the water line (solution line) and below the water line (solution line) so that no further repair is practical.

It is an object of the invention to provide a novel anode which not only minimizes manganese dioxide formation but also shows greatly reduced corrosion at the solution line portion.

In accordance with the present invention, corrosion of the anode at the solution line is so greatly reduced that said corrosion occurs at about the same rate at the solution line portion as the rate of underwater corrosion, i. e. the rate of corrosion at the portions below the solution line portion.

It is a further object to realize the economy flowing from the advantages of the invention.

In accordance with the invention, a composite lead alloy anode is provided, consisting essentially of two portions, a body portion which in use may be wholly submerged in the electrolyte, an upper or solution line portion which in use is partly submerged and partly not submerged in the electrolyte, the body portion being a lead silver alloy composed of silver 0.75 to 0.95% and the balance lead and said upper or solution line portion being a lead-silver-arsenic alloy composed of about 1% silver, about 1% arsenic and the balance lead.

The invention will be defined in the claims and further described with reference to the accompanying drawing in which is shown diagrammatically:

In Fig. 1 a cross section of the cell at one of the anolyte portions thereof.

In Fig. 2 a somewhat enlarged section on line **2—2**, Fig. 1.

In Fig. 3 a partial or fragmentary view of one of the anolyte portions showing a different form of anode structure.

In Fig. 4 a somewhat enlarged section on line **4—4**, Fig. 3.

In Fig. 5 a partial and somewhat enlarged sectional view of another form of anode structure.

In Fig. 1, the copper conductor or cross bar **1** has ends supported on the upper edges of sides **2** of the tank, one end making electrical contact with the positive or anode bus bar **3** of the D. C. electrical circuit. Insulation strips **4** may also be provided as shown. Sheet lead strip or tongue **5** may be wrapped around and fused or "burned" onto the copper bar for excellent electrical contact and protection against corrosion. Preferably, however, the tongue or strip **5** is cast around the cross bar **3**. **6** is the solution or electrolyte level or "water line." Each of the three composite anodes essentially of two portions, a body portion **7** and a "solution line" portion **8**, the two portions being fused together. Just above the "water line" or solution line the solution line portions of each of the three anodes are welded onto the depending or hanging lead sheet **5**. The solution line portion **8** overlaps the solution line **6** top and bottom and is an alloy composed of about 1% silver, about 1% arsenic, balance lead. The body portions **7** are composed of 0.75% silver balance lead. A side view of the construction is shown in Fig. 2.

The "solution" line portion **8** shown in Figs. 1 and 2 may be applied as a welded on or "overlap" portion to a new anode having the composition 0.75% to 0.95% silver balance lead or to a used anode having that composition and corroded at the "water line" or solution line.

Figs. 3 and 4 show the preferred form of the invention in which the solution line portion **8** is welded to the body portion **7**, the latter having an end portion **7*a*** extending beyond the solution line portion **8** and being welded to the lead tongue **5** at the point **5*a*** thereof.

In the form illustrated in Fig. 5, the solution line portion **8** is not an overlay but is a preformed strip welded or fused to the body portion **7** and **9** and to the lead tongue **5** at **10**.

The flat anode body portions **7** are provided with openings, defined by edges **11**, passing through said body portions as one means of controlling the effective surface area so that the anode current density is about 150–200 percent of the cathode current density, e. g. 60–100 amperes per square foot of anode surface. Said openings may, however, be omitted and the desired total effective anode area otherwise obtained.

This new construction eliminates the disastrous solution line corrosion of the 0.75% silver balance lead alloy and the composite structure shows lives with no repair for solution line corrosion of 140 weeks or more as compared to 35 weeks for the 1% silver, 1% arsenic, balance lead alloy or about 21 to 40 weeks for the 0.75% silver balance lead alloy.

In commercial plant runs water line corrosion of the 0.75% silver balance lead alloy anodes has been their most serious drawback. Normally the 0.75% silver balance lead alloy anodes require water line repair about every two or three cleaning cycles or every 14 to 21 weeks. Without repair corrosion at the solution line would ultimately cause failure of the anode, with all or most of the anode dropping into the solution at the end of approximately 40 weeks.

In one test of an 0.75% silver balance lead alloy the anode sections were cast solid in a closed mold and holes were then drilled in anode sections. Water line corrosion was severe and was eliminated with application of a 1% silver, 1% arsenic, balance lead alloy overlay. Life of this test set of anodes was 140 weeks.

The voltage difference, considered as a galvanic cell, of the 0.75% silver balance lead alloy and the 1% silver, 1% arsenic, balance lead alloy with anolyte is so small as to be negligible so that there is no evidence of galvanic corrosion or crevice corrosion at their junctions.

The alloy compositions of the anode body portion have been described as silver 0.75% balance lead or silver 0.75 to 0.95% balance lead and the silver and arsenic contents of the solution line portion have been described as silver about 1%, arsenic about 1%, balance lead.

Permissive and preferred ranges of the silver contents of the body portion are shown as follows:

	Silver Content of Body Portion
Permissive ---------- percent	0.50 to 2.4
Preferred ---------- do	0.75 to .95

Permissive and preferred ranges of the silver and arsenic contents of the solution line portion are shown as follows:

	Silver and Arsenic Contents of Solution Line Portion	
	Silver, percent	Arsenic, percent
Permissive	0.50 to 2.4	0.25 to 2.5.
Preferred	0.75 to .95	0.5 to 1.00.

The balance of the alloys other than silver, or silver and arsenic, respectively, is lead and incidental impurities.

I claim:

1. A composite anode for the electrowinning of manganese comprising an elongated body portion and a solution line portion fused thereto adjacent one end, said body portion being a silver lead alloy consisting of silver 0.50% to 2.4% and the balance lead, and said solution line portion being a lead silver arsenic alloy consisting of silver 0.50% to 2.4%, arsenic 0.25%, to 2.5% balance lead.

2. A composite anode for the electrowinning of manganese comprising an elongated body portion and a solution line portion fused thereto adjacent one end, said body portion being a silver lead alloy consisting of silver 0.75% to 0.95% balance lead, and said solution line portion being a lead silver arsenic alloy consisting of silver 0.75% to 0.95%, arsenic 0.5% to 1.00%, balance lead.

3. A composite anode for the electrowinning of manganese comprising an elongated body portion and a solution line portion fused thereto adjacent one end, said body portion being a silver lead alloy consisting of silver 0.50 to 2.4% and the balance lead, and said solution line portion being a lead silver arsenic alloy consisting of silver 0.50% to 2.4%, arsenic 0.25% to 2.5%, balance lead, the solution line portion extending circumferentially around the body portion.

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