July 12, 1966 G. P. HENEGAR 3,260,662

ANODE ASSEMBLY FOR MERCURY CATHODE CELLS

Filed Feb. 13, 1962

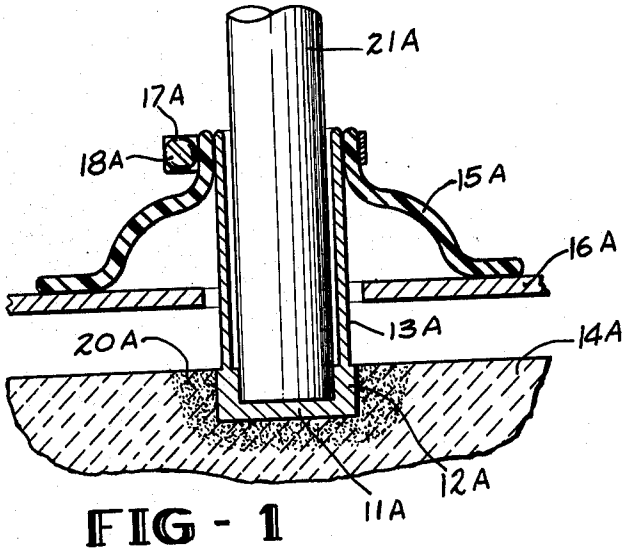


FIG - 1

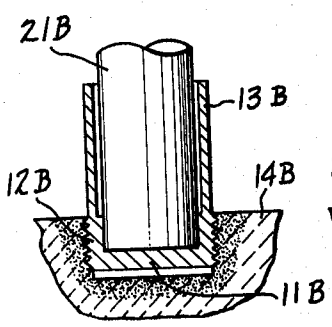


FIG - 2

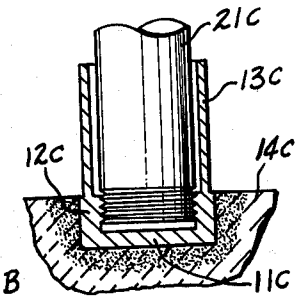


FIG - 3

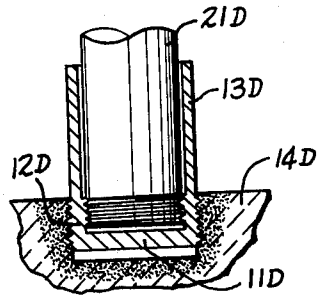


FIG - 4

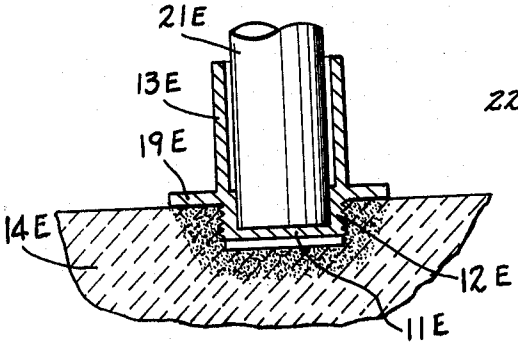


FIG - 5

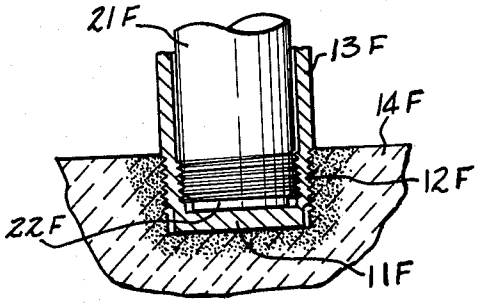


FIG - 6

INVENTOR:
GLEN P. HENEGAR
BY Gordon D. Byrket
AGENT

United States Patent Office 3,260,662 Patented July 12, 1966

3,260,662

ANODE ASSEMBLY FOR MERCURY CATHODE CELLS

Glen P. Henegar, Saltville, Va., assignor to Olin Mathieson Chemical Corporation, a corporation of Virginia

Filed Feb. 13, 1962, Ser. No. 173,070
6 Claims. (Cl. 204—279)

This invention relates to electrolytic alkali-chlorine cells of the mercury cathode type. More particularly the invention relates to an improved structure for supporting the anode and for protecting the lead-in from the corrosive action of cell gases.

Anodes are conventionally suspended in the electrolyzer chamber of mercury cells by means permitting adjustment of the elevation of the anodes with respect to the bottom of the cell and the mercury cathode flowing thereon. The lead-in serves to conduct the electric current from outside the cell, usually from a bus bar, to the anode inside the cell. The lead-in also usually serves to support the anode and is appropriately threaded or otherwise designed to permit frequent and close adjustment of the elevation of the anode.

Various materials have been used for lead-in structures but the primary considerations are cost, structural strength and high electrical conductivity. Cupreous metals, including particularly copper and brass, are particularly preferred as lead-in materials satisfying these three primary requirements. However, copper and brass are rapidly attacked by the moist chlorine gas inside the cell and must be protected therefrom. U.S. Patent 2,328,665 refers to an insulator sleeve around that portion of the lead-in which passes through the aperture in the cover primarily to avoid electrical contact of the lead-in with other structures. U.S. Patent 2,627,501 describes a porcelain pipe concentrically around the lead-in to seal off the lead-in from contact with anode gases and the electrolyte. Porcelain sleeves suffer from the defect of fragility and are likely to crack in use partly due to uneven heating and partly to attempts to tighten the joints at the upper and lower ends of the sleeve to avoid gas leakage.

In prior structures the weight of the anode is carried by the lead-in which has been attached by various means to the anode. Under the severe service conditions in mercury cells in the presence of elevated temperatures, water and water vapor, chlorine and hydrochloric acid gas, the joint between the lead-in and the anode is a frequent source of mechanical failure, allowing the anode to incline or drop to the bottom of the cell, or electrical failure, developing increased resistance across the joint or permitting short circuits if the anode contacts the mercury cathode. The sleeves of the prior art have aggravated these difficulties by increasing the mechanical pressure on the anode lead-in joint in attempts to effect a gas-tight seal of the sleeve against the anode. The sleeve of the present invention, in contrast, effects the complete protection of the lead-in from the action of cell-gases, contributes to the support of the anode instead of aggravating the problem, and eliminates at least one of the joints between the lead-in and the graphite anode. Advantageously, the graphite anodes are impregnated with oil in the vicinity of the lead-in joint to render the anodes impervious to chlorine and to prevent its deleterious action on graphite threads.

The titanium sleeves of the present invention are fabricated in a manner which has the advantage of avoiding the necessity for a seal between the lead-in and the upper end of the sleeve and also avoiding the necessity for a lead button or other means of contact between the lead-in and the graphite anode. It co-operates with the lead-in to support the anode in the cell and provides better electrical contact while eliminating one cause of electrical and mechanical failure, namely, the usual lead button.

The sleeve of the present invention comprises a titanium tube with thick walls near one end and closed at that end by a flat button of titanium. The thick walled portion of the sleeve is a minor proportion of the total length of the sleeve and may be, for example, from about ½ to ½ inches in a total length of 3 to 8 inches. The thin walled portion of the sleeve is appropriately fabricated of titanium tubes of any appropriate diameter to accommodate the lead-in leaving a concentric air space between the two. The air space usually amounts to about 1/16 to 3/8 inch. Tubing of 1/16, to 3/32, or 1/8 inch in wall thickness are commercially available and suitable for this purpose. The walls of the tubing may be thickened at one end by mechanical working, closed by means of a flat sheet of titanium welded onto the thickened walls and machined as described below. Alternatively and preferably, the thick walled portion of the sleeve is fabricated from a section of tubing having thicker walls and smaller internal diameter than the thin walled portion of the sleeve. The heavier tubing is closed at one end by welding thereto a disc of titanium, machining the inner and outer walls and welding the thicker walled section to the thinner walled section. In another mode, the thick walled section may be fabricated from a solid billet of titanium, removing most of the center portion to form a cup having a bottom and side walls, forming the inner and outer walls of the cup to receive the lead-in and to engage the anode, respectively.

The inside diameter of the thick walled portion of the sleeve is less than that of the thin walled portion of the sleeve in order to assemble the post by sliding the sleeve over the lead-in until the inner surface of the thick walled portion engages the lead-in. The inner wall of the thick wall portion of the sleeve is machined to provide for press fitting or interference fitting the lead-in into the thick wall portion. Alternatively the thick wall portion of the sleeve and the lower end of the lead-in are threaded and thus tightly engaged. The outer surface of the thick walled portion of the sleeve is machined for press fitting or interference fitting into a recess in the graphite anode or is threaded into a correspondingly threaded recess in the graphite anode. The lead-in is completely enclosed by the titanium sleeve except that the lead-in protrudes from the top and the assembly is supported by threads clamps or in any conventional manner.

Improved electrical contact can be obtained, if desired, by modifying the shape of the inserted end of the lead-in and of the closed end of the sleeve to provide a stub of reduced diameter on both the lead-in and the bottom of the sleeve. When the lead-in is threaded into the sleeve and the sleeve in turn is threaded into the recess in the graphite anode, larger areas of contact are provided for electrical conductance.

The titanium sleeves have the advantage over porcelain or alumina that they will not crack, they are

not sensitive to temperature changes and they can readily be fabricated with the necessary precision. They are superior to other metal sleeves in their complete resistance to any action by wet chlorine gas. Compared to plastic materials they do not creep or flow. Where there is any possibility of contact with cell gases with the lead-in it is completely protected by titanium since the lower end of the sleeve is capped by titanium.

While the above description refers particularly to titanium, it is to be understood that tantalum is equally satisfactory for fabrication of the protective sleeves of the present invention. Tantalum suffers mainly from its present high cost. Alloys in which titanium or tantalum are the principal constitutents are also useful, including titanium silicide, $TiSi_2$ in which the titanium amounts to a little more than 45 percent. Generally titanium, tantalum and alloys in which they are the principal constituents and which exhibit corrosion resistant properties comparable to titanium and tantalum in the environment of the present invention are suitable.

Graphite anodes are conventional in the art and the present invention is admirably adapted thereto. However, the invention is not limited thereto and is also useful with anodes of other suitable materials, including metals, particularly platinum, titanium, tantalum and platinized titanium, for example.

Attached FIGURE 1 shows an anode assembly of the present invention in which the lead-in is interference fitted into the sleeve and the sleeve in turn is interference fitted into the graphite anode. The sleeve consists of bottom **11A**, thick walled portion **12A**, and thin walled portion **13A**. Lead-in **21A** is concentrically interference fitted into portion **12A** until it contacts bottom **11A** of the sleeve. The thin walled part **13A** has a slightly greater internal diameter than that of the thick walled portion **12A**. The assembled lead-in **21A** and sleeve is interference fitted into the recess in graphite anode **14A**. The oil impregnated portion of the anode is indicated at **20A**. A flexible rubber boot **15A** is attached to cell cover **16A** and, by means of clamp **17A**, tightened by screw **18A** to the upper portion of the sleeve.

FIGURE 2 shows a modification in which lead-in **21B** is interference fitted into the thick walled portion **12B** of the sleeve having thin walled portion **13B**. The thick walled portion **12B** is externally threaded and screwed into a correspondingly threaded recess in anode **14B**. The bottom **11B** of the sleeve does not quite contact the bottom of the recess in anode **14B**.

FIGURE 3 shows a modification in which lead-in **21C** is threaded into the internally threaded thick walled portion **12C**. The thick walled portion **12C** is externally machined for interference fitting into a recess in anode **14C**. The bottom of the sleeve is indicated at **11C** and the thin walled portion at **13C**.

FIGURE 4 shows a modification in which the thick walled portion **12D** of the sleeve is threaded internally and externally to receive correspondingly threaded lead-in **21D** and to screw into a correspondingly threaded recess in anode **14D**. The bottom of the sleeve is shown at **11D** and the thin walled portion at **13D**.

FIGURE 5 adds a flange **19E** to the thick walled portion **12E** of sleeve. The thick walled portion **12E** is externally threaded to fit a correspondingly threaded recess in anode **14E**. Lead-in **21E** is interference fitted into the thick walled portion **12E**. The bottom of the sleeve is shown at **11E** and the thin walled portion at **13E**. The anode is shown at **14E**. The flange **19E** provides added protection and strength to the threads.

FIGURE 6 shows a modification in which a stub **22F** of reduced diameter is provided at the end of the lead-in **21F** and the bottom of the sleeve **11F** has a stub of reduced diameter. When the threaded lead-in is tightened into threaded thick walled portion **12F** of the sleeve, stub **22F** is brought into good electrical contact with bottom **11F** of the sleeve. Similarly when the threaded

thick walled portion **12F** of the sleeve is tightened into threaded recess in graphite anode **14F**, bottom **11F** is brought into good electrical contact with the graphite. The thin walled portion of the sleeve is shown at **13F**.

Example I

Anode assemblies were fabricated in the style of FIGURE 2. For the thin walled portion, titanium tube having an outside diameter of 2¼ inches with a wall thickness of 3/32 inch was used. To one end of each tube was welded a section of titanium tube having an outside diameter of 2½ inches. This thick walled portion was closed by welding a circular plate of titanium ⅛ inch thick to the open end of the larger tube. The thick walled portion was externally threaded to fit a correspondingly threaded recess in graphite anodes 16 x 16 x 6 inches. Brass pipe, 1¾ inches in diameter was intereference fitted under 5,000 p.s.i. pressure into the inside of the thick walled portion which had an inside diameter 0.006 inch less than the brass pipe. The anode post assemblies were fitted with flexible boots and suspended in operating mercury cells. In operation, including regular adjustment of the interelectrode distances, the titanium sleeves and brass lead-ins were completely unattacked. None of the anodes were "lost" by dropping to the bottom of the cell and none were tilted or short-circuited by shifting at the anode-lead-in joint.

Example II

Several titanium sleeves of the style of FIGURE 4 were fabricated of titanium tube having an outside diameter of 2¼ inches with a wall thickness of 3/32 inch. To one end of each tube was welded a titanium cup turned from a solid billet of titanium having a diameter of 2½ inches. The center was cut out leaving a cup having a bottom ⅛ inch thick and a wall which, when internally threaded, fit corresponding threads on 1¾ inch brass pipe. The thick walled portion was externally threaded to fit a correspondingly threaded, oil impregnated recess in a graphite anode. The anode post assemblies were fitted with flexible boots and suspended in operating mercury cells. Each titanium-to-graphite joint carried a current of approximately 1000 amperes. The voltage drop across the joint varied as follows:

Time, days:	Voltage drop
Original	0.000222
67	.001130
98	.001180
133	.000986
162	.001000

After the initial change, no further increase in voltage appeared during this test. This stability compares favorably with the steadily increasing voltage drop frequently found with other joints.

What is claimed is:

1. An anode assembly for mercury cells comprising a graphite anode having a cylindrical recess in its upper surface, a cupreous metal lead-in and a tubular sleeve surrounding the lead-in, said tubular sleeve having a thin walled portion and, near one end, a thick walled portion of smaller internal diameter than the thin walled portion, said sleeve open at the end having the thin walled portion and closed by a flat bottom at the end having the thick walled portion, said lead-in fitted internally into the thick walled portion with clearance between said lead-in and the thin walled portion of the sleeve, said thick walled portion fitted internally into the recess in said anode, said tubular sleeve composed of a metal selected from the group consisting of titanium, tantalum and alloys in which said metals are the principal constituents and which exhibit corrosion resistant properties comparable to titanium and tantalum.

2. The anode assembly of claim 1 in which the thick walled portion of the sleeve is internally threaded to receive corresponding threads on the lead-in.

3. The anode assembly of claim 1 in which the thick walled portion of the sleeve is externally threaded to engage corresponding threads in the recess in the anode.

4. The anode assembly of claim 1 in which the thick walled portion of the sleeve is internally adapted to receive the lead-in by interference fitting and externally threaded to engage corresponding threads in the recess in the anode.

5. The anode assembly of claim 1 in which the sleeve additonally has an external flange perpendicular to the axis of the sleeve at the junction of the thick walled portion and the thin walled portion of said sleeve.

6. The anode assembly of claim 1 in which the sleeve is composed of titanium.

References Cited by the Examiner

UNITED STATES PATENTS

2,328,665	9/1943	Munson	204—286
2,986,513	5/1961	Ornhjelm	204—286
3,037,928	6/1962	Hass	204—286
3,080,310	3/1963	Lindenmaier	204—286

FOREIGN PATENTS

616,029	3/1961	Canada.
124,423	11/1958	U.S.S.R.

JOHN H. MACK, *Primary Examiner.*

D. R. JORDAN, *Assistant Examiner.*