Patented Mar. 27, 1951 2,546,548

# UNITED STATES PATENT OFFICE

2,546,548

## ANODE FOR ELECTROWINNING MANGANESE AND METHOD OF MAKING THE SAME

John Koster, Crimora, Va., assignor to Crimora Research & Development Corporation, Crimora, Va., a corporation of Virginia

No Drawing. Application June 23, 1945, Serial No. 601,326

3 Claims. (Cl. 204—56)

1

This invention relates to anodes for the electrowinning of manganese. It has for its object the provision of anodes of lead alloys on which may be formed an adherent coating composed essentially of manganese and lead oxides. This has been accomplished in the past by the use of certain alloys of lead, such as lead with 1% silver and lead with 1% silver and 1% arsenic. Such alloys are relatively expensive and must be used at relatively high current densities. Furthermore, they require certain preforming before they are effective in reducing the formation of manganese dioxide at the anode during the electrolytic production of manganese.

It is the purpose of the present invention to provide an anode which requires a considerably reduced period of preforming and which can be used over a wider range of current density and also one which is relatively inexpensive. Another object is to make anodes composed of elongated particles dispersed in lead alloys more effective by orienting the particles. The anodes of the prior art, such as the lead-silver and lead-silver-arsenic anodes, have been made only by casting hypoeutectic alloys, that is, homogeneous liquid metals which separate crystals of lead and their eutectics.

In accordance with this invention, small particles of relatively hard material substantially insoluble in liquid lead are dispersed in liquid lead. The mixture of fine, reatively hard, insoluble particles, and the liquid lead is then allowed to solidify and the solidified mass used as an anode either with or without further shaping. Alternatively, the relatively hard, insoluble particles may be mixed with or imbedded in solid lead and the solid mixture formed into an anode. However, the anode may be formed by pressing the particles into the surfaces of a matrix consisting substantially of lead. It is preferred, however, to use a mixture of the particles with liquid lead, because, in this way, a more uniform mixture can be obtained and the process is likewise less expensive. It is believed that the action of these relatively hard insoluble particles is to provide tentacles, or protrusions, on the surfaces of the anodes as the lead is corroded away. The tentacles hold the coating of manganese and lead oxides to a sufficient thickness, so that they are effective in protecting the anode itself from corrosion. In accordance with this conception, the preferred fine particles would be formed of materials having a relatively high mechanical strength and toughness and also a great resistance to electrolytic corrosion. In order that

2

the particles may be firmly held in the lead matrix, it is also desirable that they be wetted by the lead matrix. The particulate material added to the lead may also be formed in the molten lead itself. For example, nickel and antimony may be separately added to the lead in order to form insoluble particles of nickel antimonide. As another example, tungsten may be dissolved up to 10% in molten lead at 700° C. On cooling, idiomorphic crystals of tungsten will separate. Molybdenum behaves similarly to tungsten. As still another example, platinum or palladium may be added to lead to form an intermetallic compound therewith which will separate on cooling. For convenience of discussion, the materials which may be added to lead, in accordance with this invention, may be divided into four classes:

1. Hard insoluble nonmetallic particles, such as silica, alumina, feldspar and mica.

2. Relatively hard and corrosion-resistant metallic particles, such as chromium, stainless steel, nickel silicide, zirconium, titanium, tantalum, thorium, cobalt and stellite.

3. Intermetallic compounds formed by combining the constituents in molten lead, such as nickel antimonide, and silver antimonide, and lead platinide.

4. Metals like tungsten and molybdenum, which separate idiomorphically on cooling the lead.

In the application of this invention, when using materials of the first class, it is difficult to obtain a uniform mixing of the particles with the lead. This can be accomplished best by mixing the fine nonmetallic particles into the molten lead matrix under a vacuum, since the nonmetallic particles are not wetted by lead and tend to retain an envelope of air.

In the case of the second class of particles, namely, metallic particles, it is important to bring about the wetting of these particles by the lead, in order to insure a more uniform dispersion of particles through the lead, a greater stability of this dispersion and a more firm anchoring of the particles into the lead matrix. In order to bring about this wetting, it is desirable to add certain alloys like tin in a relatively small amount to the lead matrix. It is still more effective to give the particles a very thin coating of tin or tin-lead alloy. This process of tinning may be accomplished by the use of the usual tinning or soldering fluxes, or it may be accomplished by the electrolytic deposition of a thin coating of tin. Alternatively, the particles may be wetted with lead by the addition of a small amount of

phosphorus to the lead. These expedients for wetting metals with lead or alloys consisting substantially of lead are well known in the art of soldering and lead coating of metals. Any of the expedients known and used in those arts may be applied here to bring about an effective union between the lead matrix and the metallic particles, which are incorporated therein. The processes of powder metallurgy are also available for the production of a dispersion of fine particles of any suitable material in lead; that is to say, powdered lead and granules of the added material may be pressed into sheet form to provide anode plates. It is contemplated that coatings of such dispersions of hard metallic particles in a lead matrix might be made by the simultaneous spray coating of a suitable anode base with lead and some metallic materials, such as stainless steel stellite or silver.

In using the third and fourth classes of fine particles, namely, those which are formed in the lead matrix, the particles are, of course, wetted by the molten lead. This is an entirely satisfactory method of carrying out the principles of this invention.

Anodes which have been formed by any of the procedures which have been described may be cast and are preferably used in the cast condition. However, it is possible to work mechanically many of the dispersions of fine particles in lead which have been described, even if the dispersed material is brittle. The amount and size of dispersed material which may be used is not critical. From 1–10% is a satisfactory amount, and the size may be from 10–200-mesh or finer.

Anodes formed in accordance with this invention may be advantageously pretreated so as to provide a surface wherein the hard, relatively insoluble particles protrude from the surface so as to hold the coating which is formed in electrolysis. This treatment may consist of scratch brushing to wear away the softer lead matrix or electrolytic corrosion to corrode away the lead matrix and leave the particles in relief.

It is contemplated that certain advantages may be gained by using elongated particles for dispersion in lead, in accordance with this invention. When such elongated particles are used they are preferably arranged so that their long axis is normal to the face of the anode. This may be accomplished in a variety of ways, for example, by casting the face of the anode against a cooled surface. Also, when the particles are magnetic, the anode may be cast in a suitably arranged magnetic field. Particles may also be oriented in an electrostatic field.

While the invention has been illustrated by the addition of particles to substantially pure lead, it is contemplated that any corrosion-resistant alloy, composed substantially of lead, may be used and that the addition of fine particles of material in accordance with this invention will improve its performance as an anode in the electrowinning of manganese.



Obviously the invention is not restricted to the particular forms thereof, herein transscribed, but is capable of a wide variety of modifications within the scope of the appended claims.

What is claimed is:

1. In the preparation of an anode for electrowinning manganese, the steps of dispersing fine particles of hand, corrosion-resistant, non-metallic material of sizes between 10 mesh and 200 mesh in a base made substantially of lead; forming said dispersion into suitable shape for use as an anode; and subjecting the anode to preliminary electrolytic treatment in a manganese electrolyte to convert some of the lead on the surfaces into lead oxide and simultaneously depositing manganese dioxide thereon, thereby forming anchored, adherent coatings of said oxides on the surfaces of the anode.

2. A pre-formed anode for electrowinning manganese, comprising a plate consisting substantially of lead having partially imbedded therein dispersed, fine granular particles of an inorganic, hard corrosion-resistant, and non-metallic substance; and thin coatings of manganese dioxide and lead oxide electro-deposited on and firmly anchored to said plate by said particles.

3. An anode, as set forth in claim 2, wherein the plate contains 1% to 10% by volume of the granular particles and wherein the particles are of sizes from 10 to 200 mesh.

JOHN KOSTER.


## REFERENCES CITED

The following references are of record in the file of this patent:

### UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 190,115 | Babcock | May 1, 1877 |
| 224,078 | Copeland | Feb. 3, 1880 |
| 539,669 | Clark | May 21, 1895 |
| 627,573 | Connor | June 27, 1889 |
| 1,119,443 | Messick | Dec. 1, 1914 |
| 1,276,614 | Beusch | Aug. 20, 1918 |
| 2,145,746 | Armstrong | Jan. 31, 1939 |
| 2,159,982 | Bullock | May 30, 1939 |
| 2,320,773 | Fink | June 1, 1943 |
| 2,397,831 | Bellamy | Apr. 2, 1946 |

### FOREIGN PATENTS

| Number | Country | Date |
|---|---|---|
| 7,561 | Great Britain | 1886 |
| 147,685 | Great Britain | July 8, 1920 |
| 155,810 | Great Britain | Aug. 11, 1921 |