Patented Mar. 1, 1932 1,848,002

UNITED STATES PATENT OFFICE

JOHN R. CAIN, OF WASHINGTON, DISTRICT OF COLUMBIA, ASSIGNOR TO THE RICHARDSON COMPANY, OF LOCKLAND, OHIO, A CORPORATION OF OHIO

ANODE FOR IRON PLATING

No Drawing. Application filed March 8, 1927. Serial No. 173,793.

My invention relates to the production of anodes which are suitable for the production of electrolytic iron which is soft and workable instead of being brittle.

The problem of production of electrolytic iron involves among other things, the fact that past commercial practices have resulted in producing this iron in a brittle, non-ductile form, so far as they have come to my attention.

In a series of experiments aimed at discovering the reasons for this brittleness, and after elimination by such experiments of a number of possible causes, I have discovered that with ferrous chloride electrolytes, kept at a temperature close to the boiling point thereof, and controlled as to hydrogen ion content during the electrolytic deposition of metal, that a soft white electrolytic iron will be produced.

In a co-pending application, Serial No. 238,232, I have described an electrolytic process producing soft iron involving the continuous control of the hydrogen ion content of a ferrous electrolyte which is kept at a temperature close to the boiling point thereof during use. My anodes as here claimed are particularly adapted for use in that process.

I do not wish to limit the application of my present invention, which lies in the composition of the anode used by me to maintain the bath free of acid, to the specific type of electrolyte with which it may be employed.

The essence of my invention is the employment of a control substance as part of or as all of the anode. This invention has many advantages besides the reduction of acid development and content, and the consequent diminution of the hydrogen ion concentration as an active factor at the cathode, where the iron is being deposited.

I prefer to use ferrous sulphide (FeS) for the control substance. For one thing, ferric sulphide is an inexpensive natural substance which can be readily fused in a container, and when so fused, passes readily to the desirable ferrous condition, and can be employed to retain masses of iron or steel scrap, and of iron ores and sponge iron. Also, it has the effect of precipitating from the bath, such metals as nickel, cobalt, copper, etc., which appear in most of the scrap iron of to-day, and in many iron ores. It will result in precipitating tin, for example, thus making economically possible the use of tin cans made of tin plate, as a scrap, in connection with the process.

While I have worked out a theory upon which I base the action of my new anodes, I do not wish to be bound to the correctness thereof, since the reactions in the baths used as electrolytes by me, are not easy to trace.

I will, in the description of a typical example of my invention, however, refer to my theory of reactions, and of cause and effect, with the understanding that there may be other factors entering into the explanation of the surprising results obtained, which factors I have not as yet determined.

With the aim of producing a deposit of soft and ductile electrolytic iron upon a suitable cathode, in my typical example, I employ a cathode in the form of a sheet of electrolytic iron of the type produced by me, or resulting from annealing and pickling of electrolytic iron produced by other processes.

I employ as an electrolyte a bath of ferrous chloride in water, having 100 grams of iron per liter. This is not as concentrated a solution as I could use with good results, but will suffice for excellent work.

This electrolyte I maintain at between 90 and 95 degrees Centigrade, and I also provide for filtering the electrolyte during use, for reasons to be explained.

If an anode of iron were used, it would be necessary to add ferrous sulphide or some other neutralizer or conditioner to the bath, from time to time to obtain the effects that I obtain, and it is the object of my invention to provide an anode which automatically takes care at least in part of the iron sulphide addition, and continuously.

The probable effect of the sulphide is to react with ferric chloride, formed in part because the anodic iron is not quantitatively dissolved, and to reduce this ferric chloride to the ferrous state. Expressed as a formula, it would be $2FeCl_3$ plus FeS equals $3FeCl_2$ plus

S. The sulphide may also neutralize sulphur or chlorine acids directly formed, but I believe that its chief function is to prevent the formation of acid which would otherwise result from the hydrolysis of free ferric chloride.

A variety of processes may be used in producing the iron sulphide bearing anodes. One way will be to employ commercial iron sulphide, which will be mixed in with pieces of various sizes of iron and steel scrap, sheet clippings, borings, or other iron scrap material, in a suitable dish, which may be formed of ingot iron sheets. The dish is then placed in a furnace and heated sufficiently to sinter the mass. If ferrous sulphide is used, this fusion or sintering will be very rapid; but if the ferric form is employed, I prefer to prolong the heating until all or nearly all of the sulphide is present in the ferrous form. If it is not desired to use the dish as a part of the anode, the sintered or fused mass can be removed and will be self supporting to a degree sufficient to permit of its being used as an anode. I may prefer to use a cast anode member of iron sulphide alone, or a composite member of iron sulphide and a preformed iron core. Fused FeS has a good conductivity, and is quite effective in producing the correct neutrality of electrolyte required for depositing ductile iron.

So far I have not obtained effective results where the electrolyte is used cold.

Another form of the anode is made by using a dish of iron or steel, and fusing the iron sulphide into it, alone, in which case the dish forms a part of the anode, or the molded block may be removed therefrom and used by itself. Or I may make a composite anode including oxides of iron thus: The iron sulphide may be liquefied by the use of an oxy-acetylene torch, and the ferrous oxide of iron, or other iron, stirred into the mass, after which it is permitted to set.

I find that the "conditioning" of the electrolyte by the use of sulphide of iron in the anode itself, is much preferable to the use of same as other than part of the anode. The electrolyte not only becomes more quickly conditioned, but also keeps the proper hydrogen ion concentration longer after the conditioner has been removed.

I find also that the sulphide anodes may be used only part of the time, and can be replaced by iron anodes without sulphide, periodically, during a plating process without having ill effects upon the softness or product.

With another electrolyte the neutralizer would, perhaps, have to be different in composition, and I do not wish to limit my invention to this one substance in its broader aspects.

I may, without ill effects, in a plating apparatus having a continuous circulatory system for the electrolyte, establish a series of cells, in one of which I may use a sulphide anode, while employing only iron anodes in the next, etc. I find that the conditioning effect I have described persists for a considerable period of use of the electrolyte before further conditioning is necessary.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent, is:—

1. A solid, unitary anode for use in plating iron which consists of fused ferrous sulphide.

2. A solid unitary anode for use in plating iron which contains iron sulphide as an essential ingredient of the unitary mass.

3. A solid anode for use in plating iron which contains ferrous sulphide as an essential ingredient, together with iron the several ingredients forming a unitary, conductive mass.

4. An anode for use in plating iron which contains iron sulphide, and iron bearing materials held in said sulphide as a binding agent.

5. An anode for use in plating iron which is formed of a mass of iron bearing materials with sintered iron sulphide.

JOHN R. CAIN.