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PROCESS FOR ELECTRODEPOSITING IRON

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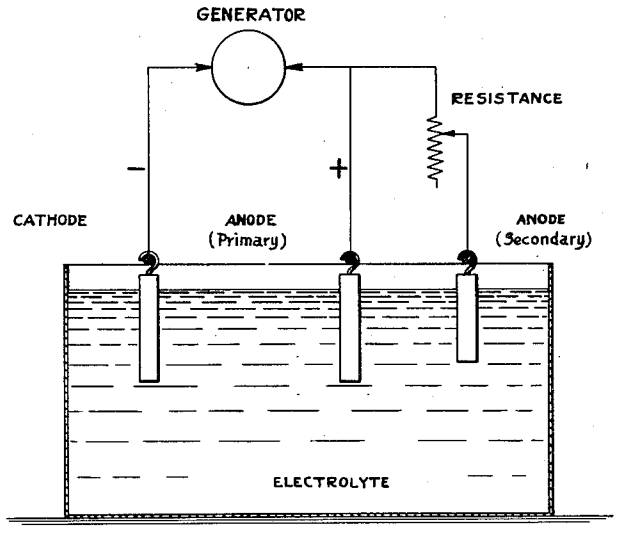

Fig. 1

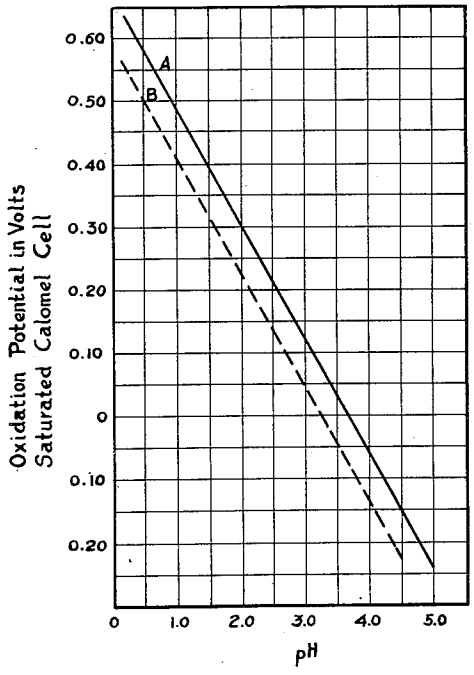

Fig. 2

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PROCESS FOR ELECTRODEPOSITING IRON

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6 Claims. (Cl. 204—48)

This invention relates to the electrodeposition of iron and more particularly it relates to an improved electrolyte and process of operating same for the continuous disposition of smooth, dense, heavy deposits of iron.

This case is a continuation-in-part of our application Serial No. 320,546, filed February 24, 1940.

In prior practices of electrodeposition, and particularly the electrodeposition of iron, many objectionable conditions have been encountered. For example, it has been general practice to require a periodic reconditioning of the electrolyte. Other prior practices required the use of multicell tank equipment in which the electrolyte was circulated. Separate anode and cathode compartments have been used and periodic filtering of the electrolyte was common practice. Roughness or "treeing" associated with heavy iron electrodeposits has been a frequent objectionable condition in conventional methods of electrodepositing iron. The occurrence of pin holes or porosity has been a common result in prior practices, particularly when it was desired to obtain a rapid electrodeposition of the iron. Solution buffers have also been employed in an attempt to provide an electrolyte which could be operated continuously.

In accordance with the practice of our invention, we have found that by maintaining the electrolyte within critical operating limits, it is possible to obtain a rapid electrodeposition of iron in a continuous operation and resulting in the formation of smooth, dense, heavy deposits of iron. Where electrodeposited iron is used in the formation of molds, dies, patterns and the like, it is essential that the deposited metal be smooth and dense in order to attain the high fidelity required in forming a replica from an original pattern. It is also necessary that such deposits be relatively heavy so as to be self-sustaining and capable of rough handling. The requirement of strength is also a factor in the manufacture of electrodeposited molds, dies and the like.

It is generally recognized that an electrolyte giving a good iron deposit is an aqueous solution of ferrous iron, ferric iron, and free hydrochloric acid with or without supplementary buffers. It has been demonstrated that the iron in such an electrolyte is deposited primarily from the ferrous state and that ferric iron is necessary only in a small amount to act as a depolarizer for hydrogen liberated at the cathode. The maximum ferric ion in the solution is regulated by the amount of acid present and since a certain minimum concentration of ferric ion is necessary, we have found that the ratio of ferric to ferrous ion concentration is of the utmost importance for correct iron electrodeposition.

It is, therefore, among the objects of our invention to provide an electrolyte in which the ratio of ferric to ferrous ion concentration is controlled within critical limitations; to provide an electrolyte which will perform efficiently in a single compartment tank and which will not require circulation, reconditioning or filtering; to provide an electrolyte which will remain clear throughout continuous operation and which will be substantially free of impurities or precipitated inclusions; to provide an electrolytic deposition process capable of forming continuous heavy deposits of iron up to thicknesses of ½ inch free from roughness or "treeing" to form a smooth, dense deposit without pin holes or porosity; to provide an electrolyte which is continuously operable without adding solution buffers; and, to provide an electrodeposition process which may be easily controlled and economically operated. These and other objects and advantages will appear more fully in the following detailed description when considered in connection with the accompanying drawing, in which:

Fig. 1 is a self-explanatory diagrammatic view of one form of apparatus which may be employed in the present invention; and,

Fig. 2 is a graph on which is plotted divisional curves illustrating the effect of hydrogen ion concentration on the ferrous-ferric concentration ratio of the electrolyte.

With reference to the drawing, Fig. 1 shows a self-descriptive diagrammatic electrolytic deposition apparatus applicable to the present invention and comprising generally a tank filled with an electrolyte and provided with a cathode and primary anode attached to a source of current. A pure iron anode is used to maintain the ferrous ion concentration of the electrolyte as iron is removed at the cathode. A secondary anode is employed in the form of an insoluble or carbon anode at a potential established experimentally to

maintain the ferric ion concentration within the desired limitations. The secondary anode is connected to a source of current through a variable resistance for the purpose of controlling the ferric ion concentration as hereinafter described.

As a preferred electrolyte, the following is exemplary:

Ferrous chloride ($FeCl_2.4H_2O$)	325 to 425 grams/liter
Calcium chloride ($CaCl_2$)	125 grams/liter
Ferric chloride ($FeCl_3.6H_2O$)	.0485 to 2.18 grams/liter (.01–.45 grams/liter of ferric ions)

To this solution is added a small amount of hydrochloric acid in order to adjust the pH to the desired range. The bath may be heated by conventional means and the operating temperature of the bath is preferably from 85° C. to 90° C. Calcium chloride is added to decrease evaporation of water at this temperature and also functions to some extent to increase the electrical conductivity of the bath.

In a homogeneous solution containing ions in one or more valence states, concentrations can be determined by measurement of the solution oxidation potential as recorded for example between a standard calomel cell and a gold electrode. The measurement of oxidation potential offers a practical means for observing the concentration of ferric iron in a concentrated solution of ferrous iron. This method of measurement is used because, in the range of concentrations under consideration, the ferrous ion is approximately 1000 times greater than the ferric concentration and the measurement of oxidation potential may be considered for all practical purposes a direct measurement of ferric ion concentration. In support of this measurement by oxidation potential, demonstrations have shown that in a solution containing 100 grams/liter of ferrous ion, a change in the ferric ion concentration of only .09 gram (from .01 gram/liter to .1 gram/liter) changes the oxidation potential .06 volt. Whereas in a similar solution changing the concentration of ferrous ion by as much as 50 grams changes the oxidation potential only .01 volt. Thus it is shown that small variations in the ferric ion concentration appreciably affects the oxidation potential and, therefore, offers a practical means of measurment in a concentrated solution of ferrous iron.

In a solution containing approximately 375 grams per liter of ferrous chloride, increasing the concentration of ferric chloride from .0485 gram per liter to 2.180 grams per liter changes the oxidation potential from .22 volt to .32 volt as observed between a saturated calomel electrode and a gold electrode. Current to the carbon anode is varied to maintain the oxidation potential within the correct range. The pH of the solution is adjusted with hydrochloric acid to a range of from .8 to 1.4.

The effect of the acidity or hydrogen ion concentration on the ferrous-ferric concentration ratio of the electrolyte is shown in graph Fig. 2 and it will be observed that the highest concentration of ferric ions in the solution is only obtained at the highest hydrogen ion concentration (low pH). Excess ferric ions for the conditions rigidly established by this graph are precipitated as ferric hydroxide ($Fe(OH)_3$) and removed from the active or ionic state.

This is a well recognized phenomenon in analytical chemistry and may be explained as follows. A neutral solution contains equal quantities of hydrogen (H^+) and hydroxyl (OH^-) ions. An acid solution registers a low pH and has an excess of (H^+) ions while an alkaline solution has an excess of (OH^-) ions. When a low pH solution containing ferric ions is made more alkaline the (OH^-) ions increase and, combining with ferric ions, eventually reach the saturation point for the solubility of ferric hydroxide $Fe(OH)_3$ and precipitation follows. A weak concentration of ferric ions requires a greater concentration of (OH^-) ions before precipitation is initiated and a strong concentration of ferric ions requires only a few (OH^-) ions for precipitation.

Each point on the curve in Fig. 2 represents the maximum ferric ion concentration which can exist at the corresponding pH. At any concentrations represented by points above or to the right of this curve, ferric hydroxide will precipitate and continue to do so until the ferric ion concentration in the solution has been reduced to a point on the curve. Actually, in a bath operated at 90° C. such precipitate will age causing particle growth which reduces the solubility of the precipitate. Under these conditions any ferric ion concentration represented by a point above or to the right of curve A will precipitate ferric hydroxide until the ferric concentration is reduced to a point on B. Curve A in the graph then represents the solubility of freshly precipitated ferric hydroxide at the corresponding pH while curve B represents the solubility of aged precipitate. Theoretically, the area of operation for the electrolyte free from precipitated ferric hydroxide lies under curve A; while for continued operation at elevated temperatures, the area of operation actually lies under the dotted curve. Operation above or to the right of the dotted curve may be carried on but frequent filtering of the electrolyte is necessary to obtain the degree of clarity associated with smooth, dense, inclusion-free deposits.

As an example, analyses for precipitated ferric hydroxide were made on an electrolyte, indicated below as X, disclosed as operating at a pH of 2.2 to 3.8, ferrous iron concentration of 80 to 150 grams/liter, and ferric iron concentration of .6 to 6 grams/liter as compared to an electrolyte Y operating within the area below the dotted line on the graph. The data show the presence of precipitate in X as predicated.

	pH	Fe″	Fe‴	Suspended matter
		Grams/liter	*Grams/liter*	*Grams/liter*
X	2.4	95.0	.636	1.02
Y	1.04	103	.085	None

The action of ferric ions in the iron plating electrolyte is to combine with or prevent the formation of hydrogen codeposited with iron at the cathode. This hydrogen, if not suppressed, forms gas bubbles resulting in pits and porosity in the iron deposit. It would appear that the only criterion for suppression of the hydrogen deposition would be the presence of a maximum ferric ion concentration. This, however, is not true because a high ferric ion concentration can only be maintained in solution by increasing the hydrogen ion concentration as demonstrated in graph 2 and the higher the hydrogen ion the more tendency for hydrogen to deposit. We have found that a concentration of ferric ion above .45

gram/liter must be accompanied by a hydrogen ion concentration too great for satisfactory operation. Therefore, a minimum and a maximum limit has been found for the ferric ion concentration wherein depolarization is most effective.

From the foregoing description, it is believed apparent that we have provided a novel electrodeposition process in which critical values of ferrous and ferric iron concentrations are maintained in combination with relative pH limits and ferric ion concentrations as expressed by oxidation potentials, and while we have shown and described a preferred method of practicing our invention, it is understood that it is susceptible of those modifications which appear obviously within the spirit of the invention and the scope of the appended claims.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. A method of electrodepositing iron from a prepared solution of ferrous chloride containing a ferric ion concentration of between .01 and .45 gram per liter and having a pH value of between .8 and 1.4 comprising passing current between a cathode and a soluble ferrous anode immersed in said solution, and maintaining in the solution during substantially the entire operation a ferric ion concentration and a pH value within the said range for ferric ion concentration and pH, to provide a substantially self-sustaining deposit of iron by continuous operation.

2. A method of electrodepositing iron from a prepared ferrous salt solution containing from 90 to 120 grams per liter of ferrous ions and containing a ferric ion concentration of between .01 and .45 gram per liter and having a pH value of between .8 and 1.4 comprising passing current between a cathode and a soluble ferrous anode immersed in said solution, and maintaining in the solution during substantially the entire operation a ferric ion concentration and a pH value within the said range for ferric ion concentration and pH, to provide a substantially self-sustaining deposit of iron by a continuous operation.

3. A method of electrodepositing iron from a prepared solution of ferrous chloride containing a ferric ion concentration of between .01 and .45 gram per liter and having a pH value of between .8 and 1.4 comprising passing current between a cathode and a soluble ferrous anode immersed in said solution, and maintaining in the solution during substantially the entire operation, at a temperature of between 85° C. and 90° C., a ferric ion concentration and a pH value within the said range for ferric ion concentration and pH, to provide a substantially self-sustaining deposit of iron by continuous operation.

4. A method of electrodepositing iron from a prepared ferrous salt solution containing from 90 to 120 grams per liter of ferrous ions, approximately 125 grams per liter of calcium chloride and containing a ferric ion concentration of between .01 and .45 gram per liter and having a pH value of between .3 and 1.4 comprising passing current between a cathode and a soluble ferrous anode immersed in said solution, and maintaining in the solution during substantially the entire operation a ferric ion concentration and a pH value within the said range of ferric ion concentration and pH, to provide a substantially self-sustaining deposit of iron by continuous operation.

5. A method of electrodepositing iron from a prepared ferrous salt solution containing from 90 to 120 grams per liter of ferrous ions, approximately 125 grams per liter of calcium chloride and containing a ferric ion concentration of between .01 and .45 gram per liter and having a pH value of between .3 and 1.4 comprising passing current between a cathode and a soluble ferrous anode immersed in said solution, and maintaining in the solution during substantially the entire operation, at a temperature of between 85° C. and 90° C., a ferric ion concentration and a pH value within the said range for ferric ion concentration and pH, to provide a substantially self-sustaining deposit of iron by continuous operation.

6. A method of electrodepositing iron from a prepared solution of ferrous chloride containing a ferric ion concentration of between .01 and .45 gram per liter and having a pH value of between .8 and 1.4 comprising passing current between a cathode and a soluble ferrous anode immersed in said solution, and maintaining in the solution during substantially the entire operation a ferric ion concentration and a pH value within the said range for ferric ion concentration and pH, by means of an insoluble anode to which a portion of the current is shunted, to provide a substantially self-sustaining deposit of iron by continuous operation.

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