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M. G. WHITFIELD ET AL

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PRODUCTION OF ELECTROLYTIC IRON

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Fig. 1.

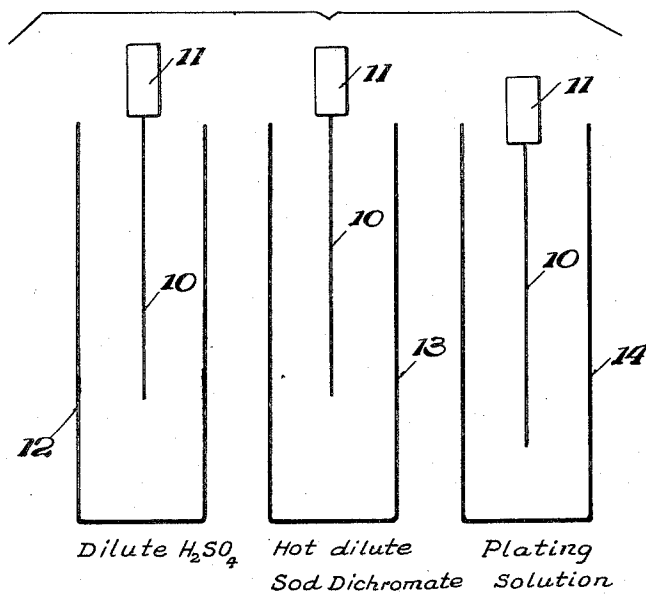


Fig. 2.

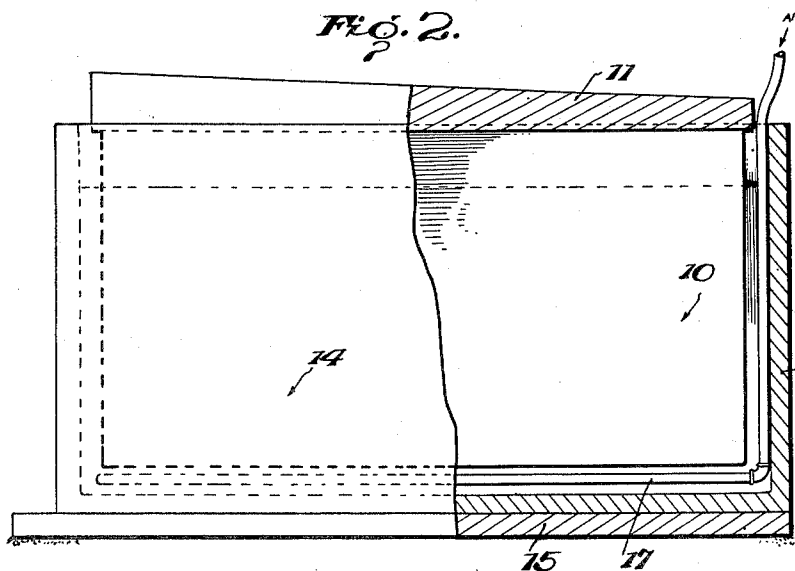
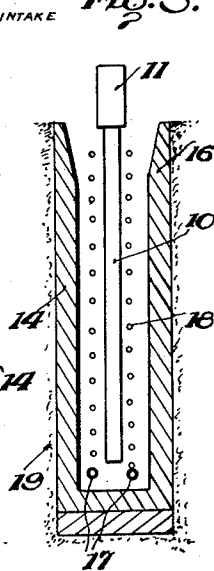


Fig. 3.



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PRODUCTION OF ELECTROLYTIC IRON

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13 Claims. (Cl. 204—1)

This invention relates to the production of electrolytic iron, and more particularly to an improved method and apparatus for producing iron sheets and other articles by electrodeposition.

5 Numerous proposals have heretofore been made as to the production of electrodeposited iron. Proposals of this character have generally involved the use of separate cells with a diaphragm therebetween to separate the catholyte from the anolyte, provisions for circulating the electrolyte through said cells, etc., and therefore have involved the use of expensive equipment. Single cell procedures have also been proposed, but these also have involved systems for circulating the electrolyte to and from reconditioning apparatus in which ferric iron has been removed or converted to ferrous iron, etc., and therefore have still involved the use of a complicated and expensive system.

20 It is an object of this invention to provide a method and apparatus for the electrodeposition of iron which involves only the use of a single cell and which also avoids the complication and expense incident to the use of a system for circulating the electrolyte to and from the cell to recondition the same.

25 Another object of this invention is to provide a method and apparatus for the electrodeposition of iron which eliminates the need for an expensive electroplating tank.

30 Another object of this invention is to provide a method and apparatus for the electrodeposition of iron which facilitates the location of the anode closely adjacent the cathode so that only a very low voltage drop exists therebetween.

35 Another object of this invention is to provide an improved electrolyte for use in the electrodeposition of iron.

40 Another object of this invention is to provide a method for electrodepositing iron which does not require aeration of the electrolyte exteriorly of the electrodeposition bath.

45 Another object of this invention is to provide a method of electrodepositing iron which is relatively continuous in character, so that the periods when the electroplating apparatus is out of service are reduced to a minimum and, if preferred, continuous deposition in the form of a continuous strip is facilitated.

50 Another object of this invention is to provide an improved method and apparatus for electrodepositing iron whereby smooth coatings of substantially uniform thickness and free from pin holes may be obtained.

Another object of this invention is to provide an improved method and apparatus for electrodepositing iron whereby the resulting deposit is not brittle, but is possessed of sufficient ductility and strength so that the same may be readily stripped from the cathode and subsequently handled.

Another object of this invention is to provide an improved method of producing electrodeposited iron sheets which are possessed of the desired ductility.

Another object of this invention is to provide an improved method of electrodepositing iron in a single cell apparatus whereby the cell may be kept in continuous use for a relatively long period of time.

Another object of this invention is to provide an improved method for electrodepositing iron which facilitates the use of steam in transferring the electrolyte to and from the cell as for filtering, and also heating the same if desired, without improper dilution of the electrolyte.

Another object of this invention is to provide a method and apparatus for the electrodeposition of iron which enables smooth coatings of iron, free from pin holes and of substantially uniform thickness, to be produced at a relatively rapid rate with apparatus of relatively low initial and maintenance cost and with relatively high efficiency.

Another object of this invention is to provide a method and apparatus for the electrodeposition of iron which will enable the production of relatively thin ductile sheets of iron, which are smooth, of substantially uniform thickness and free from pin holes, at a relatively low cost.

Other objects will appear as the description of the invention proceeds.

The invention is capable of being carried out in a variety of ways and the apparatus thereof of receiving a variety of mechanical expressions. For purposes of exemplifying the invention, the process will be described in conjunction with the production of sheets of electrodeposited iron but, as will be readily understood by those skilled in the art, the method of this invention may be readily applied to the production of continuous strips, tubular articles and other forms of electrodeposited iron. Furthermore, for purposes of illustration, one embodiment of the preferred apparatus is illustrated diagrammatically on the accompanying drawing, but it is to be expressly understood that such illustration is for purposes of exemplification only and is not intended to be

a definition of the limits of the invention as the method thereof is not limited to the use of apparatus shown.

In the drawing:

5 Fig. 1 is a diagrammatic view of the apparatus for successive treatment of the cathode;

Fig. 2 is a side view, partly in section, of a preferred form of electroplating bath; and

10 Fig. 3 is a cross section of the bath shown in Fig. 2.

In conformity with the present invention the anode preferably takes the form of a long relatively narrow cast iron trough-like tank, the length and depth of which are selected to conform generally with the length and width of the sheet that it is desired to deposit. However, the invention in its broader aspects is not limited to the use of a cast iron tank-like anode, as the anode may take the form of a suitable tank provided at its inner faces with suitable sheets of cast iron, or the anode may be provided in other ways. Also it is within the purview of the present invention to employ suitable ore as an anode when appropriately held in trough-like or plate-like containers, etc. For simplicity and economy, however, it is preferred to avoid the initial cost of a plating tank and to use a cast iron tank itself as the anode, such type of anode also possessing other advantages as will hereinafter appear.

30 The cathode may be of any suitable type and construction, but highly satisfactory results have been obtained by using a sheet of cold rolled copper properly treated so as to have a smooth, clean surface, as hereinafter referred to in detail. However, other forms of cathode suitably treated or prepared so as to facilitate deposition thereon and stripping of the electrodeposited iron therefrom may be used if preferred.

40 The electrolyte, in conformity with the present invention, is preferably composed of an acidulated aqueous solution containing:

A suitable ferrous salt, preferably ferrous chloride (FeCl_2) in a concentrate of approximately 182 to 340 grams per liter.

45 A small percentage of a suitable ferric salt, preferably ferric chloride (FeCl_3). Highly satisfactory results have been obtained by maintaining the ferric iron at approximately 1% of the total iron present, 0.79% being the value actually used, and a value on the order of 1% appears to be the lower limit desirable to use and approximately the desirable value to use.

50 A suitable buffer, such as sodium fluoride (NaF) in a concentration not exceeding approximately 10 grams per liter. Any suitable acid as hydrochloric acid to give the electrolyte a suitable pH value. Values between 2.2 and 3.8 have been found suitable for securing the ductility sought, and the range between 2.8 and 3.2 has given excellent results.

In addition there will be in the course of progressive operation of the bath a gradual accumulation of impurities, such as phosphorous and sulphur (P_2O_5 and SO_4). For example, experience has demonstrated that these built-up impurities may accumulate to approximately 8 grams per liter of P_2O_5 and approximately 1.6 grams per liter of SO_4 at the end of three months operation, but no harmful effect from their presence has been detected if the electroplating is carried on in conformity with the present invention.

75 The pH value of the electrolyte may be varied within suitable limits, depending upon the ductility desired and other factors involved, but the range of 2.2 to 3.8 has been found practicable, while for the ductility sought the range of 2.8 to 3.2 has been found preferable. The temperature of the electrolyte is preferably kept at approximately 200°F . to obtain the desired ductility of the electrodeposited iron.

Referring more in detail to the procedure which it is preferred to follow, a cathode 10 in the form of a copper sheet having a smooth cold-rolled surface, and of a size slightly larger than the sheet which it is desired to plate, is first thoroughly degreased in any suitable way as by immersion in a caustic solution, carbon tetrachloride or other alkaline solution, with or without scouring with steel wool. It is then attached to a suitable bus bar 11 and first placed in a tank 12 containing a dilute aqueous solution of sulphuric acid, preferably of from 5% to 15% concentration. The cathode is left in the dilute sulphuric acid for a few minutes until it is thoroughly clean, the time of immersion varying with the condition of the sheet. If the sheet has been previously used as a cathode and carries particles of iron it is necessary to leave the cathode in the sulphuric acid solution somewhat longer so as to remove these particles completely. The cathode sheet is then removed from tank 12 and thoroughly washed with cold water. Thereupon it is immediately dipped, in tank 13, into a hot dilute solution of sodium bichromate, preferably of from 2% to 10% concentration, and left there for a period of about five minutes.

After removal from the sodium bichromate solution the sheet is again thoroughly washed with cold water, and small wooden strips or other insulating material is placed around the edge thereof so as to protect the edge against plating thereon. For convenience, the edge strips may take the form of slotted wooden strips that may be quickly applied to the peripheral edges of the cathode. This peripheral insulation prevents deposition on the edge portions of the cathode, and when removed after the plating has been completed the edges of the cathode sheet are exposed to facilitate stripping of the deposited iron therefrom.

A suitable electric conductor is then connected to the bus bar and the cathode is placed vertically in the plating tank 14 containing an electrolyte of the character heretofore described and having suitable connection as by bus bar 15 to the electric circuit. The plating begins as soon as the cathode touches the solution and continues while the cathode is being lowered thereinto, and it is thereafter continued for a sufficient time to obtain the desired thickness of plate. The current density is preferably maintained from 75 to 100 amperes per square foot of cathode area, and with this current density a plate approximately .012 inch thick may be obtained on each side of the cathode in a period of approximately two and one-half hours.

After the desired thickness is obtained the current is turned off and the cathode removed from the tank. The wooden strips around the edge of the cathode are then removed, and the cathode may be bent slightly to free the iron sheets therefrom, whereupon said sheets may be readily stripped from the cathode. The cathode is then ready to be returned to tank 12 for cleaning and then reuse in the plating bath after immersion in the sodium bichromate solution as heretofore described.

The sheet of iron so formed is possessed of sufficient ductility so that it can be coiled on a six inch mandrel for example, but for maximum ductility it is necessary that the sheet be annealed. It has been found that sheets made by the present invention and subjected to a temperature on the order of 1350° F. for a period of approximately thirty minutes will give the ductility desired.

In conformity with the present invention the plating bath 14 preferably takes the form of a cast iron anode in tank-like form, although as heretofore pointed out any suitable plating tank 14 may be used and the anode may be formed of plates of cast iron lining the inner faces thereof or otherwise. The cast iron anode is preferably provided with relatively thick walls, at least two inches thick but preferably thicker. Such a cast iron anode may be used until its walls become relatively thin, say one-half inch, whereupon it is replaced by a new one and the old shell is remelted. It has been found that the rate of removal of the iron wall of the anode is quite uniform, and that holes or slag spots tends to become smoothed out rather than eaten deeper. The anode walls are preferably reduced in thickness or tapered at the top, as shown at 16, where they extend above the surface of the electrolyte, so that there will be substantially no overhanging edge formed by the removal of the iron. The second bus bar, when an anode in the form of a cast iron tank is used, preferably takes the form of a flat bar 15 on which the anode rests. This facilitates a good electrical contact between the anode and bus bar because the weight of the latter helps to complete and maintain the contact.

In conformity with the present invention the electrolyte is preferably maintained in agitation throughout the period of electrodeposition. To this end suitable air pipes 17 are shown adjacent the bottom of the tank, one on each side of the normal position of the cathode, and compressed air is suitably supplied thereto so that air is constantly bubbling up through the electrolyte and thoroughly agitating the same. Said air pipes 17 are formed of suitable acid-resisting material and are preferably disposed somewhat above the bottom of the tank so as to leave a space for the collection of sediment therebeneath.

Whether the anode takes the form of a cast iron tank or iron plates appropriately supported at the sides of a suitable plating tank the spacing between the sides is preferably such that the cathode is only a short distance, say two inches, at both sides thereof, from the walls of the anode, as shown in Fig. 3, which enables a low voltage drop to be maintained therebetween. The rising bubbles of air, indicated at 18 in Fig. 3, maintain the intermediate column of electrolyte in vigorous agitation, and also help to maintain the electrolyte in proper condition, and therefore a smooth deposit of iron, free from pinholes and of substantially uniform thickness, is obtained.

It has been found that it is desirable, in order that the deposited plates be possessed of the desired ductility, that the electrodeposition be carried on at a temperature of approximately 200° F., and to this end the anode tank 14 may or may not be heat insulated, depending on the need of retaining part or all of the heat that is generated during the normal operation of the cell in order to maintain the desired temperature. A small amount of insulation has been found de-

sirable, as indicated diagrammatically at 19 so as to retain some of the heat generated during the normal operation of the cell. Operation at the aforesaid temperatures possesses the additional advantage that the cell operates as an evaporator, evaporating water at a normal rate of between four and eight gallons per hour, and this in turn enables the use of steam for forcing the electrolyte into and out of the tank when, for example, filtering of the electrolyte is found to be desirable, as the steam, which would otherwise dilute the electrolyte unduly because of condensation therein, is removed by evaporation during the operation of the cell. The evaporation from the cell also enables water or a weak acid solution to be added thereto, as when removing the sediment, washing the sheets, etc., without danger of undue dilution because of the evaporation from the cell.

As the electrodeposition proceeds it is necessary to scrape down the sides of the anode tank periodically to remove the scale of graphite, silica, etc., which is left as the iron is removed, and which would otherwise gradually accumulate until it retarded or stopped the solution of the iron. This removal of scale can be readily effected by any suitable tool such as a conventional ice chipper. If the sides of the anode are scraped down regularly, substantial uniformity of the iron content of the electrolyte solution can be maintained. The larger pieces of scale removed settle to the bottom of the tank and accumulate in the space beneath the air pipes 17, but the finer particles of foreign matter tend to accumulate in the electrolyte and in time tend to roughen the plate. Therefore, it is desirable to periodically filter the electrolyte, say after a plating time of from five to seven hours, to remove therefrom the particles suspended therein. The filtering may be effected in any suitable way. Preferably the electrolyte is pumped out of the tank, the bottom thereof flushed out, and the solution suitably filtered, as through a sand filter consisting of three or more grades of sand arranged in layers from fine to coarse. After filtration the electrolyte may be returned directly to the tank, or it may be temporarily stored in a reservoir for future use.

It has been found that the composition of the plating solution or electrolyte is of very great importance. The major constituent of the electrolyte as noted is ferrous chloride, and although more dilute solutions than 182 grams per liter have not been found to give entirely satisfactory results, investigations to date do not indicate that the ferrous chloride concentration is critical.

Ferric chloride in sufficient amount to maintain its iron at about 1% of the total iron present is preferably used, for example 0.79% has been used satisfactorily, and adding this amount after each 2½ hours of plating has been found to be important in keeping the electrolyte in good plating condition. While the electrolyte can be rejuvenated by suitable periods of aeration, and such if preferred may be used within the broader aspects of the present invention, it is preferred to utilize the ferric chloride for this purpose as thereby it becomes unnecessary to withdraw the electrolyte for rejuvenation and the equipment required to remove and aerate the electrolyte is eliminated. Therefore ferric iron must be added periodically, as it is reduced both electrically and chemically during the plating operation. In the absence of ferric iron a precipitate also tends to form as a black powdery deposit on the cathode, 75

probably due to the dissolution of sulphur or phosphorous constituents from the cast iron anode.

5 Additionally, it has been found essential to use a buffer, such as sodium fluoride, to keep the solution clear and free of a floccular white precipitate which otherwise tends to form at the pH of the electrolyte which it is desired to use, and which latter precipitate interferes with the best 10 plating conditions. The amount of buffer used has been found to be rather critical, and when using sodium fluoride as heretofore referred to should approximate ten grams per liter, as larger amounts require the addition of relatively large 15 amounts of acid to maintain the pH value within the desired range with resultant loss in the ductility of the plate.

20 The pH value of the electrolyte has also been found to be quite important as it affects both the ductility of the plate and the amount of acid consumed. A pH value between 2.8 and 3.2 has been found to give excellent results but a larger range of 2.2 to 3.8 is practicable, and other values may be available, particularly for other degrees of 25 ductility than those sought. At the optimum value little acid need be added and the control is simplified.

30 The plating is continued until the sheets formed are of the desired thickness, a two and one-half hour plating period having been found sufficient to produce iron sheets of approximately .012 inch thickness, but by increasing or decreasing the plating period satisfactory plates as thick as .015 35 inch and as thin as .002 inch have been satisfactorily produced and have been found to be relatively smooth, free from pin holes, of relatively uniform thickness, and of sufficient ductility and strength to enable ready handling thereof. While plates deposited as heretofore described have 40 sufficient ductility to stand coiling on a 6 inch mandrel, it has been found necessary for greater ductility to subject the plate to a subsequent annealing operation. Maintenance of the plates at a temperature on the order of 1350° F. for a 45 period of thirty minutes has been found to render the plates of the desired ductility.

50 It will therefore be perceived that by the present invention a method of producing electrodeposited iron has been provided which requires only the use of a single cell, without an internal diaphragm to separate the anolyte from the catholyte, and the present equipment also avoids the use of a complicated system for circulating the electrolyte, aerating or otherwise reconditioning the same in an external tank, etc., so that the apparatus required is relatively simple. While 55 filtration of the electrolyte after a period from five to seven hours is found to be desirable, this is to be contrasted with the continuous circulation to and from the plating cell required in earlier systems, and involves only a relatively simple form of filter and piping connections whereby the solution may, when necessary, be transferred thereto for filtration and thereupon 60 returned to the cell, or to a reservoir if it is desired to continue the plating by use of a different batch of electrolyte during the filtering period.

65 By use of a cast iron anode in the form of a tank the expense of a separate plating tank is avoided, and as tanks of the desired size may be readily cast and replaced as needed, and the shell of a used tank may be remelted in casting new tanks, the plating process can be carried on with a minimum equipment and without loss 70 of the iron. The use of a cast iron anode in the

form of a tank also facilitates connection of the bus bars therewith, as one connection may be established and maintained by the weight of the tank resting thereon, while the other bus bar 5 may be merely rested on the top of the tank, which if desired may include centering means therefor, as a notch in each end wall. The present invention also enables the walls of the anode to be located relatively closely to the 10 cathode, and this in turn has the advantage that the voltage drop across the electrolyte is relatively small. Hence it is possible to maintain a current density on the order of from 75 to 100 amperes per square foot for both the anode and the cathode. 15

20 Additionally, the procedure as heretofore described assures a relatively smooth deposit which is free of pinholes and of substantially uniform thickness throughout. Whereas the presence of ferric chloride other than as a mere trace has heretofore been found undesirable in the electrolyte, the present invention contemplates the maintenance of ferric chloride in the electrolyte and the periodic addition of ferric chloride to 25 the electrolyte so as to maintain at all times sufficient ferric chloride present so that the iron thereof shall approximate at least 1% of the total iron in the electrolyte. This maintains the electrolyte in good plating condition without need for external aeration, and when used in conjunction with a buffer in substantially the proportions indicated as heretofore referred to assures the absence of precipitates which by collection 30 on the cathode would interfere with the formation of a smooth and uniform deposit. By keeping said buffer at substantially the proportion heretofore indicated, little acid need be added and the pH value may be kept such as to assure a plate possessed of sufficient ductility so that it may be readily stripped from the cathode and thereafter handled without injury thereof. While a preferred buffer salt has been given by way of 35 example, any other suitable buffer may be used in suitable proportions.

40 Therefore the present invention affords a relatively simple and economical procedure by which relatively thin sheets of iron may be deposited by use of a relatively simple apparatus and procedure to obtain thin sheets of substantially uniform thickness, sufficient ductility and 45 possessed of relatively smooth surfaces free of pinholes.

50 While the invention has been particularly described with respect to its use in the plating of thin sheets on a sheet cathode, the invention in its broader aspects is not to be restricted thereto as the invention may be applied to the plating of other forms or adapted to the use of a continuously moving cathode to the end that a continuous strip of iron may be formed. While the preferred apparatus has been described with considerable particularity, it is to be expressly understood that the invention is not restricted thereto. 55 Thus while a cast iron tank anode is preferred the invention may be carried out by the use of cast iron anode plates suitably supported in a permanent tank, while air pipes disposed adjacent the bottom of the plating bath have been provided for effecting the desired circulation or agitation of the electrolyte as a preferred and 60 simple procedure for accomplishing the desired results, any other suitable form of circulating or agitating means may be used as desired, etc. Also, while preferred constituents and propor- 65 70 75

tions of the electrolyte, preferred temperatures and other features of the preferred procedure have been pointed out with considerable detail, it is to be expressly understood that changes may be made therein as will now be apparent to those skilled in the art and are contemplated within the broader aspects of the present invention. Advantage may also be taken of some of the features of the present invention without taking advantage of all of the features heretofore described. Reference is therefore to be had to the appended claims for a definition of the limits of this invention.

What is claimed is:

1. The method of making electrodeposited iron which includes circulating within a single cell an acid solution of ferrous salt and subjecting said solution to electrolysis between a cathode and a soluble anode while maintaining a buffer in said solution and from time to time increasing the ferric content of said solution by adding a ferric salt to maintain the concentration of said solution in amount sufficient to its ferric content on the order of approximately 1% of the total iron content thereof.

2. The method of making electrodeposited iron which includes circulating within a single cell an acid solution of ferrous salt and subjecting said solution to electrolysis between a cathode and a soluble anode while from time to time increasing the ferric content of said solution by adding a ferric salt to said solution in amount sufficient to maintain the concentration of its ferric content on the order of approximately 1% of the total iron content of the solution and maintaining said solution at a predetermined acidity.

3. The method of making electrodeposited iron which includes circulating within a single cell an acid solution of ferrous salt and subjecting said solution to electrolysis between a cathode and a soluble anode while maintaining in said solution sodium fluoride having a concentration not exceeding approximately 10 grams per liter and from time to time, adding a ferric salt to said solution to maintain its concentration on the order of 1%.

4. The method of making electrodeposited iron which includes circulating within a single cell an acid solution of ferrous salt and subjecting said solution to electrolysis between a cathode and a soluble anode while maintaining a buffer in said solution and from time to time adding a ferric salt to said solution to maintain its concentration on the order of 1% and agitating the solution in said cell to keep the same in motion with respect to said cathode and anode.

5. The method of making electrodeposited iron which includes circulating within a single cell an acid solution of ferrous salt and subjecting said solution to electrolysis between a cathode and a soluble anode while maintaining in said solution sodium fluoride having a concentration not exceeding approximately 10 grams per liter and from time to time adding a ferric salt to said solution to maintain its concentration on the order of 1% and maintaining said solution at a predetermined acidity.

6. The method of making electrodeposited iron which includes providing a single cell, circulating only within said cell an acid solution of ferrous salt, and subjecting a relatively thin layer of said solution between a cathode and a soluble anode to electrolysis while from time to time adding a ferric salt to said solution to maintain

the concentration of ferric iron circulating in said cell at least approximately 1% of the total iron content of the solution, maintaining a buffer therein and maintaining said solution at a predetermined acidity.

7. The method of making electrodeposited iron which includes providing a single cell, circulating only within said cell an acid solution of ferrous salt, and subjecting a relatively thin layer of said solution between a cathode and a soluble anode to electrolysis while adding from time to time to said solution ferric iron to maintain in said solution ferric iron at least approximately 1% of the total iron content of the solution and maintaining a buffer therein and holding the pH value of said solution between approximately 2.8 and 3.2.

8. The method of making electrodeposited iron which includes providing a single cell, circulating only within said cell an acid solution of ferrous salt, and subjecting a relatively thin layer of said solution between a cathode and a soluble anode to electrolysis while adding from time to time to said solution ferric iron to maintain in said solution ferric iron at least approximately 1% of the total iron content of the solution and maintaining a buffer therein and maintaining said solution at a predetermined acidity and keeping the temperature of said solution at approximately 200° F.

9. The method of making electrodeposited iron which includes providing a single cell, circulating only within said cell an acid solution of ferrous salt, and subjecting a relatively thin layer of said solution between a cathode and a soluble anode to electrolysis while adding from time to time to said solution ferric iron to said solution ferric iron at least approximately 1% of the total iron content of the solution and maintaining a buffer therein not exceeding in concentration approximately 10 grams per liter and holding the pH value of said solution between approximately 2.8 and 3.2.

10. The method of making electrodeposited iron which includes providing a single cell, circulating only within said cell an acid solution of ferrous salt, and subjecting a relatively thin layer of said solution between a cathode and a soluble anode to electrolysis while adding from time to time to said solution ferric iron to maintain in said solution ferric iron at least approximately 1% of the total iron content of the solution and maintaining a buffer therein and maintaining said solution at a predetermined acidity and maintaining a current density between said cathode and anode on the order of from 75 to 100 amperes per square foot of electrode area.

11. The method of making electrodeposited iron which includes retaining in a cell which includes a soluble iron anode an acid solution of ferrous salt and a buffer, and subjecting said solution to electrolysis while circulating said solution within said cell and adding from time to time ferric salt to said circulating solution to maintain the ferric content of said solution at approximately 1% of the total iron content thereof.

12. The method of making electrodeposited iron which includes retaining in a cell which includes a soluble iron anode an acid solution of ferrous salt and a buffer, and subjecting said solution to electrolysis while circulating said solution within said cell and adding from time to time ferric salt to said circulating solution to maintain the ferric content of said solution at approximately 1% of the total iron content there-

of and maintaining said solution at a predetermined acidity.

13. The method of making electrodeposited iron which includes circulating within a single cell an acid solution of ferrous salt and subjecting said solution to electrolysis between a cathode and a soluble anode while from time to time adding a ferric salt to said solution in amount

sufficient to maintain the concentration of its ferric content at approximately 1% of the total iron content thereof and maintaining a buffer in said solution and holding the pH value of said solution between 2.2 and 3.8.

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