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ELECTRODEPOSITION OF IRON

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This invention relates to the electrodeposition of iron and is herein described as embodied in a plating bath of improved composition with which it is possible to secure deposits which are uniformly fine-grained and smooth and possess a combination of strength and ductility not heretofore obtained in electrodeposited iron without subsequent heat treatment.

Electrodeposition of iron has in the past found relatively little practical use, due in part to the hardness and brittleness of the deposits commonly secured by this method, and in part to the difficulty of controlling the deposition to maintain the desired uniformity and consistency in the results secured.

Iron deposits have been made from solutions of ferrous salts, usually the chloride or sulfate. Deposits from the chloride have been made with fine-grained structure of good strength at the beginning of the deposition but it was found that as deposition continued the grain coarsened so that the deposit had good strength only on the surface first deposited. Deposits so made could be bent in one direction but would fracture readily if bent in the other direction. Such characteristics naturally seriously limited the use of iron deposited as described.

Furthermore, it has in the past been necessary, in order to secure an iron deposit having a reasonable degree of ductility, to carry out the deposition at temperatures from about 190 to 220 or more degrees Fahrenheit, which was in many cases found to be disadvantageous. It has also been necessary heretofore to very closely control the temperature and hydrogen ion concentration in the baths from which iron was deposited, since when a relatively small change was made in either of these conditions, great differences were found in the structure and physical properties of the resulting iron deposit.

I have now discovered that the addition of a small amount of soluble manganese to the plating bath serves to prevent a coarsening of the grain as the deposition continues, and makes possible the deposition of iron in a uniformly fine-grained and ductile form of good strength, at temperatures materially lower than heretofore required. I have also discovered that the addition of manganese to the bath appears to materially broaden the permissible operating range of temperature and hydrogen ion concentration within which it is possible to secure deposits of good strength and ductility. For instance, by the addition of manganous chloride in amounts equivalent to 1.4 grams of soluble man-

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ganese per liter to a bath containing, say 300 grams of ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), which is equivalent to about 84 grams of soluble iron, per liter, I have been able to secure an iron deposit which is truly ductile, strong, and of uniformly fine grain structure, when the bath was maintained at a temperature between 160 and 220° F. and a pH value between 1.2 and 2.6. In a ferrous sulfate bath the manganese serves to refine the grain structure but has not served to produce a deposit which is truly ductile without heat treatment, apparently because of the tendency of sulfate solutions to cause hydrogen embrittlement.

Manganese in the bath appears to be effective to refine the grain structure of electrodeposited iron when present in amounts as small as 1/10 gram of soluble manganese per liter. The effect seems to increase with increasing amounts of manganese up to about 1.4 grams per liter. Little if any advantage, however, appears to be secured by further increases in the amount, though amounts up to 17 or 20 or more grams per liter have been used successfully.

The manganese is advantageously added to the ferrous chloride and ferrous sulfate solutions in the form of manganous chloride and manganous sulfate respectively. It may, however, be added in any one of a variety of other forms, such as other salts of manganese or even salts of manganic or permanganic acid, which in the ferrous chloride or sulfate solutions react to liberate ions of divalent manganese. The use of salts such as the nitrate, formate, etc., carrying acid radicals which enter into the cathode reaction, should be avoided.

It may also be noted that the action of the manganese is apparently catalytic in nature, no evidence having been discovered to indicate that any of the manganese in the bath is consumed during the electrodeposition of the iron, or that even small amounts of manganese have been deposited with the iron.

When using the chloride solutions of the present invention, I find it advantageous to maintain therein a pH value between 1.2 and 2.6, and preferably between 1.8 and 2.3 as measured at room temperature by glass electrode equipment, the greatest ductility having been secured with a chloride bath having a pH value of about 2.0. At values near and below 1.0 there is an increasing tendency towards hydrogen embrittlement. At values near and above 3, on the other hand, the grain structure becomes coarse and the value of the present invention is largely lost. When

using a chloride solution modified according to the present invention, the required acidity is advantageously secured by addition of hydrochloric acid.

When using a sulfate bath containing manganese in accordance with the present invention, the pH of the solution is advantageously maintained at a value materially higher than in the case of a chloride bath, since at values as low as 2 the anodes are attacked with great vigor and much gas is liberated at the cathode, indicating reduced efficiency. The addition of manganese to the solution, as described, advantageously in the form of manganous sulfate, serves to impart a refined grain structure to iron deposits made from solutions having pH values from 2 up to 4.5 or more.

As in the prior art, so also in the deposition of iron from the solutions of the present invention, the higher the temperature of the bath the greater the ductility of the deposit. By the use of my improved solution, however, I find it possible to secure fine-grained ductile deposits of iron at temperatures from 30° to 50° F. lower than those heretofore required.

I have frequently observed a tendency toward pitting of the deposit, which appears to be more serious at lower temperatures; but I have found, however, that this tendency toward pitting can be prevented and the character and smoothness of the deposit greatly improved by the addition to the solution of a small amount of a sodium salt of a sulfated higher fatty alcohol. For example, the products known to the trade as "Gardinol" and "Tergitol" have been found effective in amounts approximating one gram per liter, though there appears to be nothing critical about the proportion used, and a considerable variation can apparently be made in the percentages used while still securing the advantages described. With the solution so modified I have found it possible to operate successfully securing fine-grained deposits of good strength and ductility at temperatures as low as 160° F.

As in the case of the usual baths, the current densities which may be used are higher at higher temperatures and lower at lower temperatures. For example, at temperatures above 200° F. I have been able to use current densities as high as 300 amperes per square foot; at temperatures of 170° F. 100 amperes per square foot; and at 160° F. 50 amperes per square foot.

The presence in the solution of as little as 5 milligrams of lead per liter noticeably interferes with the deposition of iron, and 250 milligrams per liter completely prevents the formation of any useful deposit. Consequently the bath used should be substantially free from lead, and the use of lead-lined tanks or other lead equipment should be avoided. Other precautions, well understood by those skilled in the art, should be taken to insure the purity of the bath, such as the use of pure chemicals and anodes, specifically such as are substantially free from such impurities as arsenic, copper, tin, lead, etc. The anodes should be enclosed, as by any of the known devices, e. g. porous cups, glass or asbestos bags, etc. to maintain the cleanliness of the solution and prevent the resulting roughening of the deposit. In case of the contamination of the bath by organic materials, treatment with an inert adsorbent material such as activated carbon, is sometimes advantageous. To avoid trouble caused by oxidation of the solution by contact with the air, it may be covered with a layer of mineral oil, molten paraffin, or the like, to prevent such contact. Further, it is frequently advantageous to subject the baths of the present invention to the "breaking-in period," well known in the art, wherein the solution is subjected to electrolysis for a short time before it is placed in service.

The following table gives the pertinent facts regarding a number of examples which illustrate the use of various solutions embodying the present invention in the formation of electrolytic iron deposits having improved grain structure and ductility.

Ex-ample No.	g./l. Fe++ as chloride	g./l. Fe++ as sulfate	g./l. Mn++ as chloride	g./l. Mn++ as sulfate	g./l. Gardinol WA	g./l. Tergitol 7	Temperature, ° F.	pH	Cur. Dens. Amp./ft. ²	Tens. Str. 1000#/in. ²	Elongation, per cent	Elong. X T. S. thousands	Remarks
1.....	84	-----	1.4	-----	-----	-----	206	$\left. \begin{smallmatrix} 1.65 \\ 1.85 \end{smallmatrix} \right\}$	100	51	44	2,244	Fine-grained smooth deposit. Unusual ductility for iron.
2.....	84	-----	1.4	-----	-----	-----	194	2.1	100	-----	-----	-----	Fine-grained ductile deposit. Badly pitted.
3.....	84	-----	1.4	-----	-----	½	194	2.1	100	-----	-----	-----	Fine-grained ductile deposit. Free from pitting.
4.....	68	-----	0.8	-----	1	-----	170	$\left. \begin{smallmatrix} 1.8 \\ 2.1 \end{smallmatrix} \right\}$	50	85	23	1,960	Smooth fine-grained unusually ductile deposit free from pitting.
5.....	68	-----	0.8	-----	1	-----	160	$\left. \begin{smallmatrix} 1.8 \\ 2.0 \end{smallmatrix} \right\}$	50	111	12.5	1,390	Smooth fine-grained ductile deposit free from pitting.
6.....	-----	60	-----	1.2	-----	½	185	3.0	100	-----	-----	-----	Smooth fine-grained deposit only slightly ductile.
7.....	84	-----	1.4	-----	-----	-----	205	$\left. \begin{smallmatrix} 1.95 \\ 2.1 \end{smallmatrix} \right\}$	100	47.5	50	2,375	Fine-grained smooth deposit. Exceptionally ductile.

The concentration of ferrous iron in the solutions may be varied over rather wide limits. Solutions containing less than 45 and more than 200 grams of iron per liter in the form of ferrous chloride have been used successfully. With the higher concentrations it is in general possible to operate at somewhat lower temperatures than with the lower concentrations.

In the foregoing table the product of percent elongation and tensile strength is included to furnish a basis of comparison of the strength-ductility properties of the deposits with the same properties of known forms of iron. This product, in the case of commercial soft irons and low carbon steels where ductility is a requirement, has a commonly accepted value of about 1,500,000.

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For example, a representative cold rolled strip steel in a soft temper, intended for forming and drawing operations where ductility is of primary importance, may have a tensile strength of about 50,000 pounds per square inch and an elongation of about 30 per cent. Use of the solutions of the present invention is thus seen to make possible the production by electrolytic deposition, of iron which amply fulfills the present day strength-ductility standards set for commercial ductile iron. Even where the deposition was carried out under conditions to yield a deposit of tensile strength which is exceptionally high for substantially pure iron, it will be noted that a good degree of ductility was nevertheless secured.

Not only do the solutions of the present invention make possible the production of uniformly smooth and fine-grained deposits, but they are also found to be materially less sensitive to variations in temperature and in hydrogen ion concentration than were those of the prior art. Therefore, with my solutions it is not necessary to maintain the extremely accurate control of temperature and pH formerly required in order to produce iron deposits of satisfactory uniformity. With these solutions, also, it is possible to substantially if not entirely eliminate the evolution of gas and to secure cathode efficiencies of 93 to 98 percent or better. Operating temperatures may be from 30 to 50 degrees F. lower than heretofore while securing an iron deposit which possesses equal or superior ductility and fineness of grain structure.

The use of my solutions is thus seen to make possible a novel combination of broad operating range of temperature and pH with fine grain, good strength, and ductility of the resulting iron deposit.

I claim:

1. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of a salt from the class consisting of ferrous chloride and ferrous sulfate which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth gram and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being between 1 and 4.5 but not sufficiently high to cause a coarse grain structure of the deposited iron.

2. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of ferrous chloride which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being between 1 and 3.

3. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of ferrous chloride which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and a manganous sulfate, the pH of the bath being between 1.2 and 2.6;

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4. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of ferrous chloride which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being between 1.8 and 2.3.

5. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of ferrous sulfate which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth gram and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being between 2 and 4.5.

6. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of ferrous sulfate which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth gram and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being about 3.

7. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of a salt from the class consisting of ferrous chloride and ferrous sulfate, and a sodium salt of a sulfated higher fatty alcohol, which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth gram and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being between 1 and 4.5 but not sufficiently high to cause a coarse grain structure of the deposited iron.

8. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of ferrous chloride and a sodium salt of a sulfated higher fatty alcohol, which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth gram and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being between 1.2 and 2.6.

9. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of a salt from the class consisting of ferrous chloride and ferrous sulfate which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth gram and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being between 1 and 4.5 but not sufficiently high to cause a coarse

grain structure of the deposited iron, maintaining the current density between twenty-five and three hundred amperes per square foot at the cathode surface, and maintaining the bath during the electrodeposition of the iron at a temperature between 160° F. and 220° F.

10. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath of an aqueous solution consisting essentially of ferrous chloride which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth and not substantially more than twenty grams per liter of soluble manganese in the form of a divalent salt from the class consisting of manganous chloride and manganous sulfate, the pH of the bath being between 1.2 and 2.6, maintaining the current density between twenty-five and three hundred amperes per square foot at the cathode surface, and maintaining the bath during the electrodeposition of the iron at a temperature between 160° F. and 220° F.

11. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath consisting essentially of an aqueous solution of ferrous chloride which comprises passing an electric current through the bath while maintaining therein, as a catalytic refining agent, at least one-tenth and not substantially more than twenty grams per liter of soluble manganese in the form of manganous chloride, the pH of the bath being between 1 and 3.

12. The process of obtaining smooth, fine-grained deposits of iron from an electrolytic bath comprising essentially a solution in water of the cations of divalent manganese and divalent iron, and anions from the class consisting of chloride and sulfate which comprises passing an electric current through the bath while maintaining the divalent manganese cations therein to the extent of at least one-tenth gram per liter and sufficient to cause grain refinement of the deposited iron, but not to an extent sufficient to cause deposition of manganese along with the deposition of iron under the deposition conditions recited, and maintaining the pH of the bath during deposition between 1 and 4.5 but not sufficiently high to cause a coarse grain structure of the deposited iron, the divalent manganese cations acting as a refining agent.

13. A plating bath for the electrodeposition of iron comprising essentially a solution in water of the cations of divalent manganese and divalent iron, and anions from the class consisting of chloride and sulfate, the divalent manganese cations acting as a catalytic refining agent and being present in an amount not less than about one-tenth gram per liter and in an amount sufficient to cause grain refinement but not in an amount sufficient to cause deposition of manganese along with the deposition of iron when an electric current is passed through the bath to cause electrodeposition of iron therefrom, the pH of the solution being between 1 and 4.5, but not sufficiently high to cause a coarse grain structure of the deposited iron.

14. A plating bath for the electrodeposition of iron comprising essentially a solution in water of the cations of divalent manganese and divalent iron, and anions from the class consisting of chloride and sulfate, the divalent manganese cations acting as a catalytic refining agent and being present in an amount between about one-tenth gram and twenty grams per liter, said bath

having a pH between 1 and 4.5, but not sufficiently high to cause a coarse grain structure of the deposited iron.

15. A plating bath for the electrodeposition of iron comprising essentially a solution in water of the cations of divalent manganese and divalent iron, and chloride anions, the divalent manganese cations acting as a catalytic refining agent and being present in an amount between about one-tenth gram and twenty grams per liter, the pH of the solution being between about 1 and 3.

16. A plating bath for the electrodeposition of iron comprising essentially a solution in water of the cations of divalent manganese and divalent iron, and chloride anions, the divalent manganese cations acting as a catalytic refining agent and being present in an amount between about one-tenth gram and twenty grams per liter, the pH of the solution being between 1.2 and 2.6.

17. A plating bath for the electrodeposition of iron comprising essentially a solution in water of the cations of divalent manganese and divalent iron, and chloride anions, the divalent manganese cations acting as a catalytic refining agent and being present in an amount between about one-tenth gram and twenty grams per liter, the pH of the solution being between 1.8 and 2.3.

18. A plating bath for the electrodeposition of iron comprising essentially a solution in water of the cations of divalent manganese and divalent iron, and sulfate anions, the divalent manganese cations acting as a catalytic refining agent and being present in an amount between about one-tenth gram and twenty grams per liter, the pH of the solution being between about 2 and 4.5.

19. A plating bath for the electrodeposition of iron comprising essentially a solution in water of the cations of divalent manganese and divalent iron, and sulfate anions, the divalent manganese cations acting as a catalytic refining agent and being present in an amount between about one-tenth gram and twenty grams per liter, the pH of the solution being about 3.

20. A plating bath for the electrodeposition of iron comprising essentially a solution in water of a sodium salt of a sulfated higher fatty alcohol, cations of divalent manganese and divalent iron, and anions from the class consisting of chloride and sulfate, the divalent manganese cations acting as a catalytic refining agent and being present in an amount not less than about one-tenth gram per liter and sufficient to cause grain refinement of the deposited iron, but not in an amount sufficient to cause deposition of manganese along with the deposition of iron when an electric current is passed through the bath to cause electrodeposition of iron therefrom, the pH of the solution being not sufficiently high to cause a coarse grain structure of the deposited iron.

21. A plating bath for the electrodeposition of iron comprising essentially a solution in water of a sodium salt of a sulfated higher fatty alcohol, cations of divalent manganese and divalent iron, and chloride anions, the divalent manganese cations acting as a catalytic refining agent and being present in an amount between about one-tenth gram and twenty grams per liter, the pH of the solution being between about 1 and 3.

22. A plating bath for the electrodeposition of iron comprising essentially a solution in water of ferrous chloride and manganous chloride, the manganous chloride being present as a catalytic refining agent and in an amount sufficient to provide between about one-tenth gram and

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twenty grams per liter of manganese, said solution having a pH between about 1 and 3.

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