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ELECTRODEPOSITION OF IRON ZINC ALLOYS

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This invention relates to the electrodeposition upon iron, steel, or metals nobler than iron of coatings of iron-zinc alloys. The invention includes deposition baths, methods of depositing the alloys and articles coated with the alloys.

In accordance with the present invention, the bath for the electrodeposition includes, besides the source of iron and zinc ions, a salt to act as a buffer to prevent decreasing acidity at the cathode, and a substance tending to prevent the precipitation of ferric hydroxide from the bath. The positive ions of the salt should be such that the base formed therewith is not dissociated. The buffer action of the positive ions in preventing substantial decrease of the acidity at the cathode ensures that the hardness and covering power of the iron-zinc alloy deposited at the cathode are not lowered.

The salt is also preferably such as to maintain the bath acid at the cathode. Preferably, the salt is an ammonium salt, such as ammonium sulphate, in which case the electrical conductivity of the bath is also increased.

The substance preventing precipitation of ferric hydroxide is preferably citric acid, although any aliphatic hydroxy-acid which will furnish the ferric ion with a chelate group can be used instead of citric acid.

The bath preferably contains a third constituent which, like the others, although not taking part in the actual deposition, assists in bringing about a successful coating with the alloys. This substance is provided in order to prevent the anode becoming passive, and is preferably an alkali metal chloride. Soluble anodes, such as iron anodes, can therefore be used, and closer control of the bath composition is attained. The alkali metal ions may also reduce pitting of the deposit to some extent.

The amounts of iron and zinc, in the form of iron and zinc salts, provided in the bath may vary extensively in accordance with the nature of the alloy requiring to be deposited. In all cases, however, it has been found that the amounts of the three constituents referred to above remain substantially constant throughout. Thus it has been found that for all baths there may be used 50–150 grams per litre of ammonium sulphate, 5–20 grams per litre of potassium chloride and 0.1–5 grams per litre of citric acid. These quantities and materials relate to a deposition bath in which the sulphates of iron and zinc are employed; in the case of a chloride bath, in which iron and zinc chlorides are used, ammonium chloride should be used in place of ammonium sulphate.

The use of a wetting agent in the deposition bath has been found useful to give a smooth deposit and to prevent pitting of the deposit. The preferred wetting agent is a sodium salt of a sulphated higher alcohol derived from a straight chain hydrocarbon, for example, the material sold under the trade name "Teepol." The use of such a wetting agent is specially advisable when a relatively high proportion of zinc is to be contained in the alloy.

The invention would be more readily understood by way of example by the following description of sample deposition baths.

The baths had, in each case, iron anodes and 118 grams of ammonium sulphate, 10 grams potassium chloride and 0.5 gram citric acid per litre of the bath. Further, all baths were operated at a temperature of 50° C. The following table gives 10 examples of different baths using different amounts of iron and zinc and tabulating the resulting proportion of zinc in the alloy and the cathode efficiency and the hardness of the deposit. The iron and zinc were present as hydrated ferrous sulphate ($FeSO_4.7H_2O$) and hydrated zinc sulphate ($ZnSO_4.7H_2O$) respectively.

Ex.	Fe (g./l.)	Zn (g./l.)	Teepol (ml./l.)	pH	C. D., A./ft.^{2}	Zn, per-cent	Cath. Eff.	Hard-ness (D. P. N.)
1	50	2	----------	1.7	200	6	82	560
2	50	5	----------	2.3	280	16	91	470
3	50	10	----------	2.3	260	31	90	370
4	50	12	----------	2.2	300	34	98	--------
5	50	15	----------	2.2	250	40	97	--------
6	50	20	0.4	1.7	200	47	93	--------
7	35	20	0.4	1.7	180	61	86	300
8	30	25	0.7	1.8	150	70	80	300
9	15	20	0.4	2.2	60	82	94	--------
10	15	25	7	2.1	50	92	85	--------

The amounts of the wetting agent "Teepol," the acidity of the bath and the current density may vary within relatively wide limits in each of the above examples. The following table gives the limits of the possible variations of these values, the current density (C. D.) being given in amperes per square foot:

Example	Teepol (ml./l.)	pH	C. D., (A./ft.^{2})
1	----------	1.6–1.9	150–400
2	----------	1.7–2.8	150–400
3	----------	1.7–2.8	150–400
4	----------	1.7–2.8	150–400
5	----------	1.7–2.8	150–400
6	0.1–5.0	1.5–2.5	150–350
7	0.1–5.0	1.5–2.5	150–250
8	0.1–2.0	1.5–2.5	100–200
9	0.1–2.0	1.7–2.5	30–100
10	1.0–30	1.7–2.5	30–250

The above examples all relate to deposition from sulphate baths. However, deposition of the zinc iron alloy can be readily effected from a chloride bath, the ammonium sulphate being replaced in this case by ammonium chloride. The following is an example of a chloride bath:

Example 11

A highly lustrous (nearly mirror bright) deposit containing about 44% zinc and of hardness 415DP4 was deposited from a bath of the following composition in grams/litre:

Ferrous chloride	177
Zinc chloride	48
Ammonium chloride	30
Potassium chloride	15
Citric acid	0.5

Conditions of deposition: pH 1.25, current density 750 amps./square foot, with vigorous stirring of the bath, temperature 50° C.

In the experiments described above, iron anodes containing only low amounts of carbon, phosphorous and metals nobler than iron were used for all compositions of the alloys deposited, additions of zinc salts being made to the bath to replenish the supply of zinc ions.

On a commercial scale, however, it would be desirable, particularly when depositing alloys having a high percentage of zinc, to use anodes of the approximate composition of the alloy being deposited. These could be prepared in a bath with separate iron and zinc anodes with individual regulation of the anode currents. To minimise the contribution of the spontaneous dissolution of zinc, the zinc anode should be small enough to ensure that, with the fraction of the amount available for zinc dissolution, the current density is 100–200 A./ft.^{2}.

Above a current density of about 300 A./ft.^{2} the zinc anode becomes "passive" and its dissolution efficiency falls sharply. If there were no objection to the extra complication, a dual anode system could, of course, be used during the plating of articles.

The higher the current density, the smaller is the zinc content of the deposit for a given iron-zinc ratio in the bath. With chloride baths, dull deposits are obtained when the current density is below about 700 amps./square foot.

With sulphate baths, the temperature should be within the range 40° C. to 100° C. Temperatures lower than 40° C. are not very practicable because of the difficulty of retaining the constituents of the bath in solution. For chloride baths, the bath temperature should lie between 25° C. and 100° C. and it appears that smaller current densities have to be used as the temperature is lowered.

What is claimed is:

1. A method for the electrodeposition of iron-zinc alloys in which the bath contains a source of iron and zinc ions, an ammonium salt, citric acid and an alkali metal chloride, different from said ammonium salt, in proportions sufficient respectively to prevent decreasing acidity at the cathode, to prevent substantial precipitation of ferric hydroxide from the bath and to prevent the anode becoming passive.

2. A method for the electrodeposition of iron-zinc alloys onto a base metal nobler than iron in which the alloy is deposited from a bath having soluble anodes and containing iron and zinc ions for the simultaneous deposition thereof on the cathode, and an ammonium salt, citric acid and an alkali metal chloride, different from said ammonium salt, in proportions sufficient respectively to prevent decreasing acidity at the cathode, to prevent substantial precipitation of ferric hydroxide from the bath and to prevent the anode becoming passive.

3. A method for the electrodeposition of iron-zinc alloys according to claim 2, in which the ammonium salt is ammonium sulphate in an amount of 50 to 150 grams per litre of the bath, the alkali metal chloride in potassium chloride in an amount of 5 to 20 grams per litre, the citric acid is present in an amount of 0.1 to 5 grams per litre and the temperature of the bath is 50° C.

4. A method for the electrodeposition of iron-zinc alloys according to claim 2, in which the bath contains iron and zinc sulphates in solution.

5. A method for the electrodeposition of iron-zinc alloys according ot claim 2, in which, for the deposition of alloys containing a relatively high proportion of zinc, the bath contains a small proportion of a sodium salt of a sulphated higher alcohol derived from a straight chain hydrocarbon.

6. A bath for the electrodeposition of iron-zinc alloys, which bath includes a source of iron ions, a source of zinc ions, 50 to 150 grams of ammonium sulphate per litre of the bath, 0.1 to 5 grams of citric acid per litre of the bath and 5 to 20 grams of potassium chloride per litre of the bath.

7. A bath for the electrodeposition of iron-zinc alloys, which bath comprises iron and zinc chlorides, 50 to 150 grams per litre of ammonium chloride, 0.1 to 5 grams per litre of citric acid and 5 to 20 grams per litre of an alkali metal chloride.

8. A bath for the electrodeposition of iron-zinc alloys, which bath comprises iron and zinc sulphates, 50 to 150 grams per litre of ammonium sulphate, 0.1 to 5 grams per litre of citric acid and 5 to 20 grams per litre of an alkali metal chloride.

9. A method for electrodeposition of iron-zinc alloys onto a base metal selected from the group consisting of iron and steel in which the alloy is deposited from a bath having soluble anodes and containing iron and zinc ions for the simultaneous deposition thereof on the cathode, and an ammonium salt, citric acid and an alkali metal chloride different from said ammonium salt in proportions sufficient respectively to prevent decreasing acidity at the cathode, to prevent substantially precipitation of ferric hydroxide from the bath and to prevent the anode becoming passive.

10. A method for the electrodeposition of iron-zinc alloys in which the bath contains a source of iron and zinc ions, an ammonium salt, an aliphatic hydroxy-acid supplying a chelate group to the ferric ion and an alkali metal chloride different from said ammonium salt in proportions sufficient respectively to prevent decreasing acidity at the cathode, to prevent substantial precipitation of ferric hydroxide from the bath and to prevent the anode becoming passive.

11. A method for the electrodeposition of iron-zinc alloys onto a base metal nobler than iron in which the alloy is deposited from a bath having soluble anodes and containing iron and zinc ions for the simultaneous deposition thereof on the cathode, and an ammonium salt, an aliphatic hydroxy-acid supplying a chelate group to the ferric ion and an alkali metal chloride different from said ammonium salt in proportions sufficient respectively to prevent decreasing acidity at the cathode, to prevent substantial precipitation of ferric hydroxide from the bath and to prevent the anode becoming passive.

12. A method for the electrodeposition of iron-zinc alloys according to claim 11, in which the ammonium salt is ammonium sulphate in an amount of 50 to 150 grams per litre of the bath, the alkali metal chloride in potassium chloride in an amount of 5 to 20 grams per litre, the aliphatic hydroxy-acid is present in an amount of 0.1 to 5 grams per litre and the temperature of the bath is 50° C.

13. A method for the electrodeposition of iron-zinc alloys according to claim 11, in which the bath contains iron and zinc sulphates in solution.

14. A method for the electrodeposition of iron-zinc alloys according to claim 11, in which, for the deposition of alloys containing a relatively high proportion of zinc, the bath contains a small proportion of a sodium salt of a sulphated higher alcohol derived from a straight chain hydrocarbon.

15. A bath for the electrodeposition of iron-zinc alloys, which bath includes a source of iron ions, a source of zinc ions, 50 to 150 grams of ammonium sulphate per litre of the bath, 0.1 to 5 grams of an aliphatic hydroxy-acid supplying a chelate group to the ferric ion per litre of the bath and 5 to 20 grams of potassium chloride per litre of the bath.

16. A bath for the electrodeposition of iron zinc alloys, which bath comprises iron and zinc chlorides, 50 to 150 grams per litre of ammonium chloride, 0.1 to 5 grams per litre of an aliphatic hydroxy-acid supplying a chelate group to the ferric ion and 5 to 20 grams per litre of an alkali metal chloride.

17. A bath for the electrodeposition of iron-zinc alloys, which bath comprises iron and zinc sulphates, 50 to 150 grams per litre of ammonium sulphate, 0.1 to 5 grams per litre of an aliphatic hydroxy-acid supplying a chelate group to the ferric ion and 5 to 20 grams per litre of an alkali metal chloride.

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