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ELECTRODEPOSITION OF IRON-ZINC ALLOYS

William H. Safranek, Columbus, Ohio, assignor, by mesne assignments, to Rockwell Spring and Axle Company, Coraopolis, Pa., a corporation of Pennsylvania

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This invention relates to electroplating. More particularly, it relates to an iron-alloy electrodeposit.

In the plating of steel parts with chromium, it is necessary to polish and then buff the surface of the steel before applying the chromium coating. Frequently, a layer of nickel is electroplated on the steel, and the nickel is then buffed before the final plating with chromium. The buffing operations are costly steps because large quantities of buffing materials are consumed, and much time is required to perform this operation.

Alternatively, a layer of copper is plated on the polished steel using special baths which produce fine-grained, leveling-type plates. A layer of nickel is then plated on the copper. The superpositioning of the fine-grained copper undercoat improves the buffability of the nickel plate, with the result that buffing costs are markedly reduced. However, the copper-plating step is nearly as costly as the savings made in the buffing operation. Also, special addition agents and equipment are required.

It has now been found that by the method and bath of this invention, a ductile and leveling-type iron-alloy plate can be electrodeposited. This iron-zinc-alloy electrodeposit fills in polishing scratches and other irregularities in the surface of the basis metal so that the plated surface is smoother than the original basis metal surface. This leveling iron-alloy plate can be overplated with bright nickel plate, such as the ductile and leveling nickel plate disclosed in copending applications Serial Nos. 368,903, filed July 20, 1953; 369,223, now abandoned, filed July 20, 1953, and 369,224, now Patent No. 2,748,-068, filed July 20, 1953. The combination of a leveling iron alloy and nickel plate completely obviates the necessity of a buffing step, since the plating operations provide an attractive final appearance, even when the polished steel surface had a roughness before plating, of 20 R. M. S. microinches or more.

Should a dull or semibright nickel be used in place of bright nickel plating, the deposition of the iron-zinc alloy prior to the nickel plating greatly improves the buffability of the dull nickel plate.

Accordingly, one of the objects of this invention is to provide a ductile iron-alloy coating.

Another object is to provide economical means for smoothing polished steel surfaces prior to plating with chromium or nickel and chromium.

A further object is to improve the corrosion protection afforded by iron electroplates by codepositing zinc or zinc and nickel with the iron.

Other objects and advantageous features will be apparent from the following detailed description.

In general, this invention relates to electrodepositing an iron-zinc alloy from an aqueous bath comprising ferrous ions and zinc ions. The electroplate produced by this process contains from 2 to 15 percent zinc, and the balance iron, and is both leveling and ductile. The plate may also contain from 3 to 16 percent nickel replacing a part of the iron.

The ferrous ions are introduced into the bath by means of iron powder or soluble ferrous salts such as ferrous sulfate, ferrous ammonium sulfate, or ferrous sulfamate. The ferrous iron concentration can vary from 20 to 100 g./l. However, a ferrous iron concentration between about 35 and 75 g./l. is preferred for best leveling and ductility.

Oxidation by air or some other oxidizing agent may cause the ferrous iron to be oxidized to ferric iron. However, the ferric iron concentration should not exceed 0.3 g./l. The build-up of the ferric iron concentration may be avoided by using a large iron anode area. It may also be desirable to immerse in the bath iron rods which are not connected to the anodes. Ferric iron in the bath will be substantially reduced to ferrous iron by reaction with these iron rods. Iron or zinc powder may also be introduced into the bath for this purpose.

The zinc may be added to the bath either in the form of zinc powder, or as a soluble zinc salt, such as zinc sulfate. The concentration of zinc in the bath depends upon the iron concentration; the ratio of zinc to iron is between 0.004 and 0.05 to 1 for depositing the ductile, leveling iron alloy containing 2 to 15 percent zinc. Thus, in a bath containing 50 g./l. ferrous iron, the zinc concentration is between 0.25 and 2.5 g./l.

In addition to iron and zinc, other metals may be added to the bath for improving the physical properties of the plate, or its corrosion resistance. For example, the addition of nickel to the bath in the form of nickel sulfate, nickel ammonium sulfate, or nickel sulfamate in amount to give a nickel-iron ratio of between 0.05 and 1.25 to 1, will result in iron-rich alloy plate containing, in addition to the zinc, about 3 to 16 percent nickel, which, in combination with the zinc assists in improving the ductility, the leveling action, and the corrosion resistance of the iron-alloy plate.

The pH of the bath is preferably adjusted to between 1.5 and 3.5 by adding sulfuric acid to reduce the pH or ammonium hydroxide to raise it, as required. The bath may be operated outside this range for short periods of time, but operating at a pH greater than about 3.5 will cause precipitation of the ferrous iron.

The temperature of the bath should be maintained at between about 100° and 220° F. for satisfactory plating. For best leveling and ductility, a temperature range of from 130° to 165° F. is preferred.

Suitable anodes for electrodepositing the alloy of this invention include iron rods containing very low carbon or low-carbon steel sheet, such as SAE 1010 or SAE 1020. Iron anodes may be used continuously for long operating periods without the necessity of cleaning or otherwise treating them. If steel anodes are used, it may be necessary to periodically remove carbon sludge formed on the surface of the anode during continuous operation. Best results are obtained by bagging the anodes with a material such as cotton duck.

It may be desirable to add to the plating bath a buffer, such as boric acid or ammonium sulfate. A wetting agent may also be used to prevent pitting in the deposits. Suitable wetting agents include sulfated oxyalcohols, such as the product made by reacting coconut alcohol with ethylene oxide, followed by sulfating with sulfuric acid. Sulfated alcohols, such as sodium lauryl sulfate may also be used.

The following examples will serve to illustrate the invention with greater particularity:

Example I

A 0.001-inch alloy plate containing about 5 percent

zinc and the balance iron was electrodeposited on steel using the following bath and plating conditions:

Ferrous sulfate [$FeSO_4 \cdot 6H_2O$]—g./l.	300.0
Boric acid [H_3BO_3]—g./l.	30.0
Sulfated oxyalcohol—g./l.	0.5
Zinc sulfate [$ZnSo_4 \cdot 7H_2O$]—g./l.	1.8
Water	Balance
pH	2.3
Temperature—° F.	135±3
Cathode current density—amp./sq. ft.	50
Anode current density—amp./sq. ft.	25
Plating time—min.	30

The workpiece was agitated by moving it in the bath 30 cycles per minute using a 1-inch stroke.

The anodes were SAE 1010 steel plate, about ½-inch thick, covered with cotton duck bags. The iron consumed by plating was replenished by the anodes. The zinc co-deposited with the iron was replenished by adding zinc powder at the rate of about 3.5 grams per 100 ampere hours of operation. Each time zinc powder was dissolved, a small quantity of sulfuric acid was added to keep the pH of the bath in the range of 2.1 to 2.4.

The resulting electroplate had a roughness of from 11 to 13 R. M. S. microinches when deposited over polished steel having a roughness of from 13 to 16 R. M. S. microinches, or an average leveling of 20 percent.

Example II

A bath was operated similar to that of Example I, except that the zinc sulfate concentration was 6.2 g./l., the pH was 2.5, and the temperature was 160±3° F.

The resulting 0.001-inch electroplate contained about 12 percent zinc, and had a roughness of from 14 to 17 R. M. S. microinches, when plated over polished steel having a roughness of from 19 to 23 R. M. S. microinches. The average reduction in roughness was 25 percent.

Example III

A 0.001-inch alloy plate containing about 2 percent zinc and the balance iron was electrodeposited on steel using the following bath and operating conditions.

Ferrous sulfamate [$Fe(SO_3NH_2)_2$]—g./l.	160.0
Boric acid [H_3BO_3]—g./l.	30.0
Zinc sulfate [$ZnSO_4 \cdot 7H_2O$]—g./l.	0.9
Water	Balance
pH	1.9
Temperature—° F.	145
Cathode current density—amp./sq. ft.	50
Anode current density—amp./sq. ft.	25
Plating time—min.	30

The workpiece was agitated by moving it in the bath 30 cycles per minute, using a 1-inch stroke.

The resulting electroplate had a roughness of from 9 to 12 R. M. S. microinches over a polished steel plate having a roughness of from 18 to 20 R. M. S. microinches, or an average leveling of 45 percent.

Example IV

A bath was operated similar to that of Example III except that 0.8 g./l. zinc sulfate was used, 0.5 g./l. sulfated oxyalcohol was added and the pH was 3.0.

The resulting 0.001-inch electroplate contained about 2 percent zinc, and had a roughness of from 9 to 11 R. M. S. microinches when plated over polished steel having a roughness of from 12 to 15 R. M. S. microinches. The average leveling was about 26 percent.

Iron plates of a corresponding thickness which contained no zinc were nonleveling.

Example V

A very good leveling and corrosion-resistant plate was produced containing 1.5 percent zinc, 16 percent nickel, and the balance iron. The bath used had the following composition:

Ferrous sulfate [$FeSO_4 \cdot 7H_2O$]—g./l.	300.0
Boric acid [H_3BO_4]—g./l.	30.0
Nickel sulfate [$NiSO_4 \cdot 7H_2O$]—g./l.	350.0
Sulfated oxyalcohol—g./l.	0.5
Zinc dust—g./l.	0.25
Water	Balance
pH	2.2
Temperature—° F.	130
Cathode current density—amp./sq. ft.	50

A comparable bath, omitting the zinc, produced plates which were highly stressed and were cracked, especially near the edges. The zinc addition reduced the stress and eliminated the cracking.

The electrodeposition of zinc with iron also resulted in a more ductile plate. Iron was plated on a ⅛-inch steel panel, and the plated panel was bent around a ½-inch diameter arbor. A bend of only five degrees caused severe cracking in the iron plate.

Similar steel panels plated with the iron-zinc alloy of this invention could be bent at least 25 degrees and usually as much as 45 degrees before the first appearance of microscopic cracks. Even after a bend of 90 degrees, the cracking of the iron-zinc alloy plating was less severe than that resulting from bending the iron plating only five degrees.

A nickel plate deposited directly on the 0.001-inch iron-zinc deposits was much easier to buff to desired brightness than nickel plated directly on polished steel. Also, a decorative chromium plate (0.00001-inch) had superior corrosion resistance when plated over the nickel, iron-zinc, polished steel combination than when plated over a nickel and polished steel alone. The following table shows the results of salt spray-fog test:

Hours of Salt-Spray Test	Polished Steel Plated With 0.001-inch Iron-Zinc Alloy Plus 0.00025-inch Nickel Plus 0.00001-inch Chromium	Polished and Buffed Steel Plated With 0.00025-inch Nickel Plus 0.00001-inch Chromium
24	5 to 15 small rust spots per square foot.	more than 25.
40	15 to 25 small rust spots per square foot.	badly rusted.

In summary, there has been disclosed a novel bath and process for electrodepositing an iron-alloy plate. The alloy plating produced by this process contains from 2 to 15 percent zinc, and the balance iron, and is a ductile and leveling plate. Additionally, the plate may contain from 3 to 16 percent nickel. Although specific examples have been given to illustrate this invention, it is not intended to be limited thereby, but only by the scope of the specification and claims.

What is claimed is:

1. The process of electrodepositing a leveling, ductile, iron-zinc-alloy plate which comprises electrolyzing an aqueous acid solution containing a ferrous compound with ferrous ion in a concentration of 20 to 100 g./l., and a zinc compound with zinc ion in a zinc-ferrous ratio of from 0.004 to 0.05.

2. The method according to claim 1 wherein the temperature of the solution is from 100° to 220° F.

3. The method according to claim 1 wherein the pH is from 1.5 to 3.5.

4. The process of electrodepositing a leveling, ductile, iron-zinc-nickel-alloy plate which comprises electrolyzing an aqueous acid solution containing a ferrous compound with ferrous ion in a concentration of 20 to 100 g./l., a zinc compound with zinc ion in a zinc-ferrous ratio of from 0.004 to 0.05, and a nickel compound with nickel ion in a nickel-ferrous ratio of from 0.05 to 1.25.

5. A composition of matter useful in the deposition of iron-zinc-alloy electroplates which comprises an aqueous

solution of a ferrous compound of from 20 to 100 g./l. ferrous ion, and a zinc compound with zinc ion in a zinc-ferrous ratio of from 0.004 to 0.05.

6. A composition of matter useful in the deposition of iron-zinc-nickel-alloy electrodeposit which comprises an aqueous solution containing a ferrous compound with ferrous ion in a concentration of 20 to 100 g./l., a zinc compound with zinc ion in a zinc-ferrous ratio of from 0.004 to 0.05, and a nickel compound with nickel ion in a nickel-ferrous ratio of from 0.05 to 1.25.

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