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ELECTRODEPOSITION OF IRON AND IRON ALLOYS

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

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This application relates to electroplating. More specifically, it relates to the electrodeposition of iron and iron-alloy electroplates which are leveling and ductile.

In the process of producing bright, mirrorlike electrodeposits, it has been found necessary to smooth the basis metal surface prior to electrodepositing thereon nickel and chromium plates. This is conventionally done by mechanical finishing operations which consume costly abrasive materials and require the services of skilled operators in order to produce acceptable finishes. The mechanical finishing is done by polishing with a series of finer and finer abrasives which gradually smoothen the rough surfaces in order that a bright, mirrorlike plating can be applied without the necessity of buffing. This is particularly true where very thin coatings of nickel are applied under chromium plating. Unless the surface of the basis material is smooth, the resulting plated finish will not be mirrorlike, but will be hazy or somewhat dull.

It has now been found that by electroplating the leveling iron or iron-alloy coating of this invention on the basis material, a smooth plated surface will be formed, on which extremely thin, bright-nickel, and chromium electroplates can be applied without the necessity for mechanical polishing before plating.

Accordingly, it is one of the objects of this invention to produce an adherent, ductile, leveling iron or iron-alloy electroplate.

It is a further object to produce an adherent electroplate with leveling power suitable as an undercoat for bright-nickel and chromium plates.

Another object is to produce an iron or iron-alloy electroplate which will improve the corrosion resistance of nickel and chromium electroplated thereon.

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

In general, this invention comprises electrolyzing a bath containing ferrous sulfate, sulfated coconut oxyalcohol, and a leveling agent selected from the group consisting of saccharin and phthalimide. Nickel sulfate and zinc sulfate may be added to produce iron-nickel or iron-nickel-zinc-alloy electroplates. Also, p-toluene sulfonamide may be added to improve both leveling and brightness.

The use of saccharin and p-toluene sulfonamide as brightening agents in cid nickel baths has been disclosed in the patent to Brown, U. S. Patent No. 2,191,813. However, these compounds have been found to have no appreciable leveling action in nickel baths, and it is thus entirely unexpected that when they are used in iron and iron-alloy baths the resulting plate is leveling.

The iron plating bath of this invention comprises an aqueous solution of ferrous sulfate. Very satisfactory results can be obtained using a concentration of from 200 to 600 g./l. of ferrous iron. A preferred amount of ferrous sulfate is from 250 to 400 g./l.

For a satisfactory leveling plate, the ferric ion concentration must not be greater than 0.3 g./l. When the

ferric iron concentration does not exceed 0.15 g./l., the plates are more ductile than if this value is exceeded. The ferric ion concentration is reduced by adding iron powder or iron filings, followed by filtration.

The organic leveling agent for this bath is selected from the group consisting of saccharin and phthalimide. A preferred amount is from 2 to 3 g./l. Less than 2 g./l. of this organic agent will result in inferior leveling. An amount greater than 3 g./l. may be used, but the resulting plate will have less ductility.

The use of a wetting agent is also necessary to produce leveling plates. Very satisfactory results have been obtained by adding to the bath sulfated coconut oxyalcohol. This is formed by the reaction of coconut alcohol with ethylene oxide, followed by sulfation. The amount of wetting agent used can range from 0.025 to 0.2 g./l.

The pH of the bath may be adjusted by adding any suitable material which will not introduce undesirable materials into the bath. Examples of such materials are sulfuric acid for reducing the pH, and iron powder for raising the pH. The pH of the bath should be maintained at from 1.8 to 3.7, although a range of from 2.1 to 2.5 will result in more freedom from pitting and the formation of nodules.

During plating, the bath should be maintained at a temperature of from 120° F. to 200° F. However, better leveling is obtained within a range of from 130° F. to 165° F.

It will be obvious to those skilled in the art that the addition of a buffer such as boric acid, may be desirable. Any amount up to saturation may be used in the bath, but from 20 to 45 g./l. is preferred.

Cathode current densities used in producing the plate of this invention may range from 20 to 100 amp./sq. ft. However, the use of current densities ranging from 40 to 75 amp./sq. ft. will produce a more leveling plate and prevent burning at the edges.

Anode current densities up to 50 amp./sq. ft. may be used, although when over 40 amp./sq. ft. is used, the ferric iron concentration may build up.

Agitation during plating may be desirable. This may be accomplished by a moving work bar, a mixer, solution circulation, etc. Filtration of the plating solution may also be desirable to remove insoluble impurities.

As has been previously stated, a leveling iron-nickel-alloy plate may be produced by addition of nickel sulfate to the iron sulfate bath. Up to 250 g./l. of nickel sulfate may be added. In addition to the nickel sulfate, up to 10 g./l. zinc sulfate may also be added to the bath to produce an iron-nickel-zinc-alloy electroplate.

The leveling of the baths of this invention may be further improved by the addition of p-toluene sulfonamide in amounts up to 2.0 g./l.

The following examples show bath compositions and operating conditions to form the electroplate of this invention on a steel basis material. Iron anodes were used in all of these examples.

Example I

60	Ferrous sulfate (FeSO ₄ ·7H ₂ O)-----g./l.	300
	Saccharin -----g./l.	2.5
	Sulfated coconut oxyalcohol-----g./l.	0.05
	Boric acid (H ₃ BO ₄)-----g./l.	30
	pH -----	2.1
65	Temperature -----°F.	160
	Cathode current density-----amp./sq. ft.	50
	Anode current density-----amp./sq. ft.	25
	Filtration -----	Continuous
70	Ferric ion concentration-----g./l.	<0.3
	Plating time-----min.	25
	Leveling -----percent.	50

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Example II

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	300
Saccharin	g./l.	2
p-Toluene sulfonamide	g./l.	1.75
Sulfated coconut oxyalcohol	g./l.	0.05
Boric acid (H_3BO_4)	g./l.	31
pH		2.2
Temperature	° F.	160
Cathode current density	amp./sq. ft.	50
Anode current density	amp./sq. ft.	30
Filtration		Continuous
Ferric ion concentration, about	g./l.	0.1
Plating time	min.	25
Leveling	percent.	50

Example III

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	300
Nickel sulfate	g./l.	50
Saccharin	g./l.	3
Sulfated coconut oxyalcohol	g./l.	0.05
pH		2.3
Temperature	° F.	160
Cathode current density	amp./sq. ft.	50
Anode current density	amp./sq. ft.	25
Filtration		Continuous
Ferric ion concentration	g./l.	0.22
Plating time	min.	25
Leveling	percent.	55-58
Nickel content of plate	do.	3

Example IV

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	300
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	g./l.	90
Saccharin	g./l.	2
Sulfated coconut oxyalcohol	g./l.	0.05
Boric acid (H_3BO_4)	g./l.	30
pH		2.3
Temperature	° F.	130
Cathode current density	amp./sq. ft.	50
Anode current density	amp./sq. ft.	25
Ferric ion concentration	g./l.	<0.3
Plating time	min.	25
Leveling	percent.	26
Nickel content of plate	do.	6

Example V

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	300
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	g./l.	250
Saccharin	g./l.	2.5
Sulfated coconut oxyalcohol	g./l.	0.05
pH		2.3
Temperature	° F.	155
Cathode current density	amp./sq. ft.	50
Anode current density	amp./sq. ft.	25
Filtration		Continuous
Ferric ion concentration	g./l.	<0.3
Plating time	min.	25
Leveling	percent.	42-50
Nickel content of plate	do.	15

Example VI

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	300
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	g./l.	90
Saccharin	g./l.	2
Sulfated coconut oxyalcohol	g./l.	0.05
Boric acid (H_3BO_4)	g./l.	30
pH		3.7
Temperature	° F.	160
Cathode current density	amp./sq. ft.	50
Anode current density	amp./sq. ft.	25
Ferric ion concentration	g./l.	<0.3
Plating time	min.	25
Leveling	percent.	25

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Example VII

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	300
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	g./l.	10
Phthalimide	g./l.	1
Sulfated coconut oxyalcohol	g./l.	0.05
Boric acid (H_3BO_4)	g./l.	30
pH		2.3
Temperature	° F.	130
Cathode current density	amp./sq. ft.	50
Anode current density	amp./sq. ft.	20
Ferric ion concentration	g./l.	<0.3
Plating time	min.	25
Leveling	percent.	50

Example VIII

An electroplate was prepared under the same conditions as Example VII, except that the bath was maintained at a temperature of 160° F. during plating. Comparable results were obtained.

Example IX

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	200
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	g./l.	33
Saccharin	g./l.	2
p-Toluene sulfonamide	g./l.	1.25
Sulfated coconut oxyalcohol	g./l.	0.05
Boric acid (H_3BO_4)	g./l.	20
pH		2.2
Temperature	° F.	150
Cathode current density	amp./sq. ft.	60
Anode current density	amp./sq. ft.	30
Filtration		Continuous
Ferric ion concentration	g./l.	0.15
Plating time	min.	20
Leveling		Good
Nickel content of plate	percent.	3

Example X

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	300
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	g./l.	56
Saccharin	g./l.	2
p-Toluene sulfonamide	g./l.	1.75
Sulfated coconut oxyalcohol	g./l.	0.1
Boric acid (H_3BO_4)	g./l.	30
pH		2.1
Temperature	° F.	150
Cathode current density	amp./sq. ft.	90
Anode current density	amp./sq. ft.	45
Filtration		Continuous
Ferric ion concentration	g./l.	<0.2
Plating time	min.	20
Leveling		Good
Nickel content of plate		Not determined

Example XI

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	600
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	g./l.	106
Saccharin	g./l.	2
p-Toluene sulfonamide	g./l.	1.75
Sulfated coconut oxyalcohol	g./l.	0.05
Boric acid (H_3BO_4)	g./l.	60
pH		2.2
Temperature	° F.	150
Cathode current density	amp./sq. ft.	60
Anode current density	amp./sq. ft.	30
Filtration		Continuous
Ferric ion concentration	g./l.	0.15
Plating time	min.	20
Leveling		Good
Nickel content of plate	percent.	3

Example XII

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	300
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	g./l.	90
Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)	g./l.	7
Saccharin	g./l.	2
Sulfated coconut oxyalcohol	g./l.	0.05
Boric acid (H_3BO_3)	g./l.	30
pH		2.3
Temperature	°F.	160
Cathode current density	amp./sq. ft.	50
Anode current density	amp./sq. ft.	25
Ferric ion concentration	g./l.	<0.3
Plating time	min.	25
Leveling	percent	40-50

The plates produced by all of the foregoing examples were bright, smooth, pit-free, and adherent. As a result of the leveling action, they are capable of being plated further with bright nickel and chromium to produce a brilliant, mirrorlike surface.

It has been further discovered that the plating of this invention results in unusual resistance to corrosion when overlaid with nickel and chromium. Steel coated with the plate produced by Example IV (6% nickel) was covered with 0.0001 inch bright nickel and 0.00001 inch chromium. No excessive rusting was noticed after 50 hours of salt-spray testing. When the steel was coated with 0.001 inch of a conventional iron-nickel alloy (15% nickel) and the same amount of nickel and chromium, the steel was protected for only 14 to 40 hours salt-spray testing.

Steel coated with the plating of Example I, plus 0.0003 inch of bright nickel, plus 0.00001 inch of chromium, resisted excessive rusting for 84 hours of salt-spray testing, while the same amount of nickel and chromium protected the steel for only 49 hours.

As can be seen from the foregoing specification, there has been disclosed a novel method for producing a leveling coating of iron and iron alloys wherein the roughness of the basis material can be materially reduced without resorting to mechanical smoothing operations. The quantitative data on leveling given in the above examples refer to the reduction in roughness measured by a diamond point surface analyzer in terms of R. M. S. micro-inches. It has further been disclosed that the iron and iron-alloy plates of this invention afford superior protection against corrosion for the basis material when overlaid with nickel and chromium.

What is claimed is:

1. The process of electrodepositing a plating selected from the group consisting of iron and iron base alloys which comprises electrolyzing an aqueous solution containing predominantly ferrous sulfate, a minor amount of an organic compound selected from the group consisting of saccharin and phthalimide and a small quantity of a wetting agent, said amount and quantity being sufficient to provide a level and ductile plate.

2. The process of electrodepositing a plating selected from the group consisting of iron and iron base alloys which comprises electrolyzing an aqueous solution containing predominantly ferrous sulfate, a minor amount of an organic compound selected from the group consisting of saccharin and phthalimide, and a small quantity of sulfated coconut oxyalcohol, said amount and quantity being sufficient to provide a level and ductile plate.

3. The process of electrodepositing a plating selected from the group consisting of iron and iron base alloys which comprises electrolyzing an aqueous solution containing predominantly ferrous sulfate, 2 to 3 g./l. of an organic compound selected from the group consisting of

saccharin and phthalimide, and 0.025 to 0.2 g./l. of sulfated coconut oxyalcohol.

4. A composition of matter for electrodepositing a plating selected from the group consisting of iron and iron base alloys which comprises an aqueous solution containing predominantly ferrous sulfate, a minor amount of an organic compound selected from the group consisting of saccharin and phthalimide, and a small quantity of a wetting agent, said amount and quantity being sufficient to provide a level and ductile plate.

5. A composition of matter for electrodepositing a plating selected from the group consisting of iron and iron base alloys which comprises an aqueous solution containing predominantly ferrous sulfate, a minor amount of an organic compound selected from the group consisting of saccharin and phthalimide, and a small quantity of sulfated coconut oxyalcohol, said amount and quantity being sufficient to provide a level and ductile plate.

6. A composition of matter for electrodepositing a plating selected from the group consisting of iron and iron base alloys which comprises an aqueous solution containing predominantly ferrous sulfate, 2 to 3 g./l. of an organic compound selected from the group consisting of saccharin and phthalimide, and 0.025 to 0.2 g./l. of sulfated coconut oxyalcohol.

7. The process of electrodepositing a plating selected from the group consisting of iron and iron base alloys which comprises electrolyzing an aqueous solution containing from 250 to 400 g./l. of ferrous sulfate, 2 to 3 g./l. of an organic compound selected from the group consisting of saccharin and phthalimide, and 0.025 to 0.2 g./l. of sulfated coconut oxyalcohol.

8. A composition of matter for electrodepositing a plating selected from the group consisting of iron and iron base alloys which comprises an aqueous solution containing from 250 to 400 g./l. ferrous sulfate, 2 to 3 g./l. of an organic compound selected from the group consisting of saccharin and phthalimide, and 0.025 to 0.2 g./l. of sulfated coconut oxyalcohol.

9. The process according to claim 2 wherein the aqueous solution additionally contains nickel sulfate.

10. The process according to claim 9 wherein the aqueous solution additionally contains zinc sulfate.

11. The process according to claim 2 wherein the aqueous solution additionally contains p-toluene sulfonamide.

12. The process according to claim 9 wherein the aqueous solution additionally contains p-toluene sulfonamide.

13. The process according to claim 10 wherein the aqueous solution additionally contains p-toluene sulfonamide.

14. The composition according to claim 5 containing additionally nickel sulfate.

15. The composition according to claim 14 containing additionally zinc sulfate.

16. The composition according to claim 5 containing additionally p-toluene sulfonamide.

17. The composition according to claim 14 containing additionally p-toluene sulfonamide.

18. The composition according to claim 15 containing additionally p-toluene sulfonamide.

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