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2,822,326

BRIGHT CHROMIUM ALLOY PLATING

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This invention relates to chromium-alloy coatings. More particularly, it relates to a method or process of electrodepositing coatings of chromium alloys having a bright and lustrous surface, and to the bath used and the coatings produced thereby.

It has been found that suitable trivalent chromium baths can be used to electrodeposit chromium or chromium alloy plate with a high degree of success. In U. S. Patent 2,693,444, there has been disclosed a chromium-alloy plating bath containing chromium ammonium sulfate, magnesium sulfate, ammonium sulfate, sodium sulfite, salts of alloy metals, ammonium hydroxide, and water. Other baths containing trivalent chromium ions, ions capable of conducting an electric current, and ions of alloy metals are disclosed in copending application Serial No. 487,697. Although the plates acquired by the baths of these two disclosures vary as to brightness, they must all be mechanically buffed to a considerable extent to obtain a commercially acceptable bright and lustrous finish.

Except as a result of mechanical buffing, no method was previously known for producing bright chromium-alloy plates, particularly chromium-iron and chromium-nickel plates. Although many brightening agents have been discovered for copper, nickel, zinc, and other plating baths, representative agents of these classes of brightening agents either do not cause chromium-iron or chromium-nickel plate to be brightened, or greatly reduce cathode efficiency to an intolerable or impossible value.

Buffing of electroplates is a costly operation. Chromium-iron alloy plate is particularly hard to buff and is excessively costly.

It has now been discovered that by the process and bath of this invention, an electrodeposited coating from trivalent chromium baths can be produced, which overcomes the undesirable features of the prior-art electroplates.

Accordingly, one of the objects of this invention is to provide a smooth, bright, and lustrous chromium-alloy coat.

Another object is to reduce or eliminate the mechanical buffing heretofore required for brightening chromium-alloy electroplates.

Another object is to provide a method for brightening chromium-alloy plate as it is electrodeposited.

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

In general, the process of this invention relates to electrolyzing an aqueous bath containing trivalent chromium ions, ions capable of conducting an electric current, ions of alloying metals plus additions of supplementary brightening agents for effecting bright plates. Specifically, the addition agents of this invention are the principal organic ammonia derivatives, namely the amines and amides. Best results are obtained while using the following organic ammonia derivatives: methyl pyridium chloride, diamino pyridine, formamide, urea, dimethyl-

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thiourea, histidine monohydrochloride, and sulfonated saccharin.

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

Example I

An aqueous bath of the following composition was prepared:

	G./l.
10 Chromium ammonium sulfate $[\text{Cr}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 24\text{H}_2\text{O}]$	300
Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$	150
Ferrous ammonium sulfate $[\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}]$	5.0
15 Methyl pyridium chloride	0.5

The methyl pyridium chloride was a supplementary brightening agent. A steel panel was immersed in the bath as the cathode, while the anode was constructed of a chromium-iron alloy (85% Cr, 15% Fe). The bath was maintained at a temperature of 115° F., having a pH of from 1.8 to 2.0. The cathode current density was 200 amperes per square foot and the anode current density was approximately 60 amperes per square foot. The cathode efficiency was 29 percent. The leveling action of the plates was about 30 percent per 0.0005 inch of plate. The coating was found to comprise about 85 percent chromium and 15 percent iron.

The appearance of the resulting plate was mirror-bright and very smooth.

Example II

A bath was prepared similar to that used in Example I except that instead of methyl pyridium chloride being added as a brightening agent 0.1 g./l. of diamino pyridine was used. The cathode current density was 100 amperes per square foot and the anode current density was about 250 amperes per square foot. A platinum anode was used instead of the chromium-iron alloy. Otherwise, operating conditions were about the same.

The coating was found to comprise about 85 percent chromium and 15 percent iron. The appearance of the resulting plate was semibright and smooth.

Example III

A bath was prepared similar to that used in Example I except that, instead of methyl pyridium chloride being added as a brightening agent, 0.5 percent by volume of 4,4'-diamino diphenylamine 2 sulfonic acid was used. The cathode current density was about 70 amperes per square foot while the anode current density was about 250 amperes per square foot. A platinum anode was used. Otherwise, operating conditions were about the same.

The coating was found to comprise about 85 percent chromium and 15 percent iron. The appearance of the resulting plate was semibright and smooth.

Example IV

A bath was prepared similar to that used in Example I except that instead of methyl pyridium chloride being added as a brightening agent 1.0 percent by volume formamide was used. The cathode current density was about 100 amperes per square foot while the anode current density was about 250 amperes per square foot. A platinum anode was used. Otherwise, operating conditions were about the same.

The coating was found to comprise about 85 percent chromium and 15 percent iron. The appearance of the resulting plate was semibright and smooth.

Example V

A similar deposit of about 94 percent chromium and

the balance iron was obtained from the following aqueous solution:

	G./l.
Basic chromium sulfate $[\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{O} \cdot 5\text{H}_2\text{O}]$...	450
Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$	50
Ferrous ammonium sulfate $[\text{Fe}(\text{NH}_4)_2 \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$...	13
Urea	6

The urea was the supplementary brightening agent. The bath was maintained at a temperature of from 115° F. to 118° F., with a pH of from 1.9 to 2.0. The anode was made of a chromium-iron alloy. The cathode current density was from 300 to 400 amperes per square foot while the anode current density was approximately 100 amperes per square foot. The cathode efficiency was from 26 to 34 percent.

The resulting plate exhibited a semibright and smooth surface.

Example VI

A deposit of about 75 percent chromium and 25 percent iron was obtained from the following aqueous solution:

	G./l.
Basic chromium sulfate $[\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{O} \cdot 5\text{H}_2\text{O}]$...	450
Ferrous sulfate $[\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}]$	10
Urea	188

The urea was the supplementary brightening agent. The bath was maintained at 115° F. and the pH maintained at from 1.7 to 2.0. The anode was made of a chromium-iron alloy (85% Cr, 15% Fe). The cathode current density was from 300 to 400 while the anode current density was about 100 amperes per square foot. The cathode efficiency was from 22 to 26 percent.

The resulting plate exhibited a bright surface. Hardness measurements taken on samples from this bath ranged from 770 to 1098 Knoop.

Example VII

A bath was prepared similar to that used in Example VI except 50 g./l. of ammonium sulfate were added and 0.3 g./l. of dimethylthiourea was used in place of the urea. The temperature was maintained at 130° F. and the pH adjusted to from 1.5 to 1.8.

Example VIII

A deposit of about 85 percent chromium and 15 percent iron was obtained from the following solution:

	G./l.
Basic chromium sulfate $[\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{O} \cdot 5\text{H}_2\text{O}]$...	450
Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$	50
Ferrous ammonium sulfate $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$...	10
	10
Boric acid $[\text{H}_3\text{BO}_3]$	30
Dimethyl urea.....	4.0

The dimethyl urea was the supplementary brightening agent. Boric acid is added to the bath to act as a buffer and to improve smoothness of the plate. The bath was maintained at about 130° F., and the pH maintained at about 1.8. The anode was made of a chromium-iron alloy (85% Cr, 15% Fe). The cathode current density was about 75 amperes per square foot and the anode current density was about 100 amperes per square foot. The cathode efficiency was about 6 percent.

The resulting plate exhibited a semibright surface.

Example IX

A deposit of approximately 98 percent chromium and two percent nickel was obtained from the following aqueous solution:

Chromium ammonium sulfate $[\text{Cr}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}]$...	300
Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$	150
Nickel sulfate $[\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$	1.5
Sodium salt of sulfonated saccharin.....	2

The sodium salt of sulfonated saccharin was the supplementary brightening agent. The bath was maintained at about 115° F., and the pH was maintained at from 1.4 to 1.5. The anode was made of platinum. The cathode current density was from 125 to 250 amperes per square foot and the anode current density was up to 1000 amperes per square foot. The leveling action was about 40 percent per 0.0005 inch of plate.

The resulting plate was semibright and smooth.

Example X

A bath was prepared similar to that used in Example IX except that, instead of 2 g./l. of sodium salt of sulfonated saccharin being used, 4 g./l. were used. Also 3 g./l. instead of 1.5 g./l. of nickel sulfate were added. The pH was maintained at 1.6, and the cathode current density maintained at 250 amperes per square foot. Otherwise, operating conditions were the same.

The resulting plate comprised about 98 percent chromium and two percent nickel and exhibited a mirror-bright surface that was very smooth.

Example XI

A bath was prepared similar to that used in Example IX except that, instead of sodium salt of sulfonated saccharin being used as a brightening agent 0.5 g./l. of methyl pyridium chloride was used. Also 3 g./l. instead of 1.5 g./l. of nickel sulfate were added. The pH was maintained at 1.0. The cathode current density was 125 amperes per square foot and the anode current density was 500 amperes per square foot. Otherwise, operating conditions were the same.

The resulting plate comprised about 98 percent chromium and two percent nickel and exhibited a mirror-bright surface that was smooth.

Example XII

A bath was prepared similar to that used in Example IX except that, instead of sodium salt of sulfonated saccharin being used as a brightening agent 0.5 g./l. of histidine monohydrochloride was added. The pH was maintained at 1.6. The cathode current density was 150 amperes per square foot and the anode current density was 600 amperes per square foot. Otherwise, operating conditions were the same.

The resulting plate comprised about 98 percent chromium and two percent nickel and exhibited a semibright, smooth surface.

In carrying out most of the plating operations, glass tanks were used. However, it should be obvious that any material can be used that will not react with the electrolyte during the plating process. Rubber-lined steel tanks have provided to be satisfactory.

Chromium-alloy plates may be obtained from these baths by using a pH of from about 0.2 to about 3.5; however, to obtain the best results, the preferred range is from about 1.4 to 2.5. The pH may be adjusted by adding acid or alkaline reagents such as sulfuric acid or ammonium hydroxide, to the solutions. Plating baths made up of chromium ammonium sulfate, chromium potassium sulfate, chromium sulfate, are acid in nature and require initial additions of alkaline reagents, such as ammonium hydroxide, to obtain the proper pH. Trivalent chromium baths made up from basic chromium sulfate, chromium carbonate, and chromium oxide, require acid additions to obtain the proper initial pH. During operation of the baths, either those in which chromium ammonium sulfate or other trivalent chromium compounds have been added, it may be necessary to add small amounts of acid

to prevent the pH from rising. Boric acid may be added to the baths as a buffer reagent to stabilize the pH. If alkaline reagents, such as ammonium hydroxide, are added to the bath after it has been prepared, special care should be taken to avoid the formation of precipitates which are relatively insoluble.

The addition agents or brightening additions of this invention may be any of the principal organic ammonia derivatives or mixtures of the principal organic ammonia derivatives. By principal organic ammonia derivatives is meant any organic amine or amide. Best results are obtained by making additions of methyl pyridine chloride, diamino pyridine, formamide, urea, dimethylthiourea, histidine monohydrochloride, and sulfonated saccharin.

While satisfactory results can be obtained by additions of any of the preferred compounds over a range of from a trace to the saturation point of the brightening agent, best results are obtained by maintaining the concentration at from 0.1 to 10 g./l. In the case of urea, there appears to be no preferred range in that additions of from 0.1 to 180 g./l. are effective.

Trivalent chromium ions can be supplied to the plating baths by the addition of trivalent chromium compounds, such as chromium ammonium sulfate, chromium sulfate, basic chromium sulfate, chromium carbonate, chromium potassium sulfate, and chromic oxide. The amount of trivalent chromium ions used in the baths is dependent on the current density and the temperature at which the bath is operated. Satisfactory results have been obtained with concentrations ranging from 20 g./l. to saturation. However, the most satisfactory results are obtained with concentrations of from 30 to 75 g./l. If chromic oxide or chromium carbonate are used as the source of trivalent ions, additions of a sulfuric acid are necessary to provide sulfate ion concentrations which, for best results, should not be less than 80 g./l. If chromium potassium sulfate is used, the potassium ion concentration should not exceed 150 g./l.

Trivalent chromium salts are commercially prepared by reducing chromic acid or sodium dichromate with an organic reducing agent such as alcohol, molasses, or with sulfur dioxide. The product contains residual reducing agents, and oxidation products thereof, since an excess of the reducing agent is used to complete the reduction. Thus, plain solutions made up of trivalent chromium salts will contain these harmful impurities. The excess reducing agents, and oxidizing products thereof, and any other harmful impurities in the bath can be removed by the addition of a small amount of activated carbon, preferably by means of a slurry of the finely divided powder in water. The activated carbon removes the impurities by means of absorption. The purification of the plating baths by means of activated carbon results in smoother and better plates.

The alloying constituents of the plating baths are added to the bath in the form of metal salts such as iron or nickel sulfate. The valence of the alloying metals is not as important a factor in the resulting plate as is the valence of the chromium. For instance, iron may be added either as ferrous or ferric ammonium sulfate, ferrous or ferric sulfate, or by means of a mixture of ferrous and ferric salts. However, for best results, the reduced or ferrous salts are preferred. Nickel, as an alloying element may be added as nickel sulfate or nickel ammonium sulfate. The amount of alloying metal ions added to the bath is dependent on the composition of the alloy plates desired. Alloy plates can be produced that are predominantly iron or nickel in composition; however, by combining the ferrous or ferric ion concentrations to from 0.6 to 2.5 g./l., of the nickel ions to from 0.1 to 1.0 g./l., better alloy plates are obtained.

While the examples heretofore given have related only to chromium-iron and chromium-nickel alloys, the electroplating baths of this invention may also be readily

adapted to chromium-cobalt alloys. To electroplate a chromium-cobalt alloy, cobalt salts, such as cobalt ammonium sulfate, can be substituted for the ferrous or nickel compounds in the plating solution. The preferred range for cobalt ions is substantially the same as the preferred range for nickel, that is from 0.1 to 1.0 g./l.

Various ternary or even quaternary combinations of these metals can be electrodeposited in the form of hard alloy plates. For example, a bright chromium-iron-nickel alloy or a bright chromium-iron-cobalt alloy can be electrodeposited by means of the electroplating baths of this invention. Nickel or cobalt salts or both nickel and cobalt salts are added to the bath in addition to iron salts and trivalent chromium compounds to obtain ternary or quaternary bright alloy plates.

Alkali metal compounds are added to the bath to obtain improved throwing power. The term "alkali metal compound" is intended to include ammonium compound. Ammonium sulfate and sodium sulfate have proved to be satisfactory when used for this purpose, but other alkali metal compounds, such as potassium sulfate may be used as well. Ammonium compounds have proved to be the most effective for this purpose. The alkali metal compounds may be added separately or as mixtures. Addition of alkali metal compounds are particularly effective when plating is done with low current density and low concentrations of trivalent chromium ions. Concentration of the alkali metal compounds in the plating bath are dependent, to some extent, on the trivalent chromium salt or compound used. For instance, when using basic chromium sulfate, sufficient sodium sulfate may be present in the bath after dissolving this chromium salt to carry on the plating operation with further additions of alkali metal compounds. For best results, total alkali metal ion concentration should be within the concentration range of from 10 to 50 g./l. In baths where sulfate salts are employed, total sulfate ion concentrations should be within the range of from 80 to 600 g./l.

The plating bath may be operated over a wide range of temperatures providing the pH is properly adjusted. There is some danger of chrome alum or chromium ammonium sulfate precipitating from the bath where the concentration of the chromium is in excess of 70 g./l. and the temperature is allowed to drop below 110° F. The preferred temperature range for the trivalent chromium baths of this invention is from 110° F. to 130° F.

Satisfactory plating has been obtained by using current densities of from 100 to 600 amperes per square foot. The selection of the proper current density is dependent upon the concentration of the chromium and alloy salts. Other factors affecting the choice of the proper current density include the size of the plating tank, the shape and contour of the parts, and the time required to produce a given thickness.

The anode may be made of any material that will conduct an electric current and that will not react with the plating bath to adversely contaminate the plating solutions. It is preferable to use either chromium alloy anodes corresponding to the desired plate composition, or platinum, or platinum-covered silver anodes. When using chromium alloy anodes, either chromium-iron alloy or chromium-nickel alloy, it is preferable to adjust the anode current density to between 50 and 100 amperes per square foot. By this means, the metal is dissolved from the anodes at the same rate as metal is deposited on the cathodes. If platinum or platinum-covered silver anodes are used, the anode current density is not critical and may be between 50 and 1000 amperes per square foot.

When insoluble anodes are used, such as a platinum anode described above, the bath is not replenished in chromium or the alloy metal. As a result of continuous operation, the concentration of the chromium and the alloying metal will diminish proportionally with the time of electrodeposition. These metals must be constantly

replaced by addition of metal compounds, such as the trivalent chromium salts or compounds originally used, and their alloying salts or soluble metal oxide or hydrates.

It will, of course, be understood that the various details of the process may be varied without departing from the principles of this invention.

What is claimed is:

1. The method of electrodepositing a bright chromium-iron alloy plate which comprises electrolyzing an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.6 to 2.5 g./l. of iron ions, and containing additionally at least one brightening agent in the range specified selected from the group consisting of:

Brightening agent:	Range g./l.
Urea	.1-188
Methyl pyridium chloride	.1- 10
Diamino pyridine	.1- 10
Formamide	.1- 10
Dimethylthiourea	.1- 10
Histidine monohydrochloride	.1- 10
Sulfonated saccharin	.1- 10

2. The method of electrodepositing a bright chromium-nickel alloy plate which comprises electrolyzing an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.1 to 1.0 g./l. of nickel ions and containing additionally at least one brightening agent in the range specified selected from the group consisting of:

Brightening agent:	Range g./l.
Urea	.1-188
Methyl pyridium chloride	.1- 10
Diamino pyridine	.1- 10
Formamide	.1- 10
Dimethylthiourea	.1- 10
Histidine monohydrochloride	.1- 10
Sulfonated saccharin	.1- 10

3. The method of electrodepositing a bright chromium-cobalt alloy plate which comprises electrolyzing an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.1 to 1.0 g./l. of cobalt ions and containing additionally at least one brightening agent in the range specified selected from the group consisting of:

Brightening agent:	Range g./l.
Urea	.1-188
Methyl pyridium chloride	.1- 10
Diamino pyridine	.1- 10
Formamide	.1- 10
Dimethylthiourea	.1- 10
Histidine monohydrochloride	.1- 10
Sulfonated saccharin	.1- 10

4. A composition of matter for electrodepositing a chromium-iron alloy plate which comprises an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.6 to 2.5 g./l. of iron ions, and containing additionally at least one brightening agent in the range specified selected from the group consisting of:

Brightening agent:	Range g./l.
Urea	.1-188
Methyl pyridium chloride	.1- 10
Diamino pyridine	.1- 10
Formamide	.1- 10
Dimethylthiourea	.1- 10
Histidine monohydrochloride	.1- 10
Sulfonated saccharin	.1- 10

5. A composition of matter for electrodepositing a chromium-nickel alloy plate which comprises an aqueous

bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.1 to 1.0 g./l. of nickel ions and containing additionally at least one brightening agent in the range specified selected from the group consisting of:

Brightening agent:	Range g./l.
Urea	.1-188
Methyl pyridium chloride	.1- 10
Diamino pyridine	.1- 10
Formamide	.1- 10
Diamino pyridine	.1- 10
Histidine monohydrochloride	.1- 10
Sulfonated saccharin	.1- 10

6. A composition of matter for electrodepositing a chromium-cobalt alloy plate which comprises an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.1 to 1.0 g./l. of cobalt ions and containing additionally at least one brightening agent in the range specified selected from the group consisting of:

Brightening agent:	Range g./l.
Urea	.1-188
Methyl pyridium chloride	.1-10
Diamino pyridine	.1-10
Formamide	.1-10
Dimethylthiourea	.1-10
Histidine monohydrochloride	.1-10
Sulfonated saccharin	.1-10

7. The method of electrodepositing a bright chromium-alloy plate, which comprises electrolyzing an aqueous bath containing 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, the ions of at least one alloying metal selected from the group consisting of from 0.6 to 2.5 g./l. of iron ions, from 0.1 to 1.0 g./l. of nickel ions, from 0.1 to 1.0 g./l. of cobalt ions, and containing additionally at least one brightening agent in the range specified, selected from the group consisting of:

Brightening agent:	Range g./l.
Urea	.1-188
Methyl pyridium chloride	.1-10
Diamino pyridine	.1-10
Formamide	.1-10
Dimethylthiourea	.1-10
Histidine monohydrochloride	.1-10
Sulfonated saccharin	.1-10

8. A method of electrodepositing a bright chromium-alloy plate which comprises electrolyzing an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, the ions of at least one alloying metal selected from the group consisting of from 0.6 to 2.5 g./l. of iron ions, from 0.1 to 1.0 g./l. of nickel ions, and from 0.1 to 1.0 g./l. of cobalt ions, and containing additionally from .1 to 10 g./l. of sulfonated saccharin.

9. The method of electrodepositing a bright chromium-iron alloy plate which comprises electrolyzing an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.6 to 2.5 g./l. of iron ions, and containing additionally from .1 to 10 g./l. of sulfonated saccharin.

10. The method of electrodepositing a bright chromium-nickel alloy plate which comprises electrolyzing an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.1 to 1.0 g./l. of nickel ions, and containing additionally from .1 to 10 g./l. of sulfonated saccharin.

11. The method of electrodepositing a bright chromium-cobalt alloy plate which comprises electrolyzing an aqueous bath containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, 0.1 to 1.0 g./l.

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of cobalt ions, and containing additionally from .1 to 10 g./l. of sulfonated saccharin.

12. A composition of matter for electrodepositing a chromium-alloy plate, which comprises an aqueous bath containing 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, the ions of at least one alloying metal selected from the group consisting of from 0.6 to 2.5 g./l. of iron ions, from 0.1 to 1.0 g./l. of nickel ions, and from 0.1 to 1.0 g./l. of cobalt ions, and containing additionally at least one brightening agent in the range specified, selected from the group consisting of:

Brightening agent:	Range g./l.	
Urea1-188	
Methyl pyridium chloride1-10	5
Diamino pyridine1-10	
Formamide1-10	
Dimethylthiourea1-10	
Histidine monohydrochloride1-10	
Sulfonated saccharin1-10	20

13. A composition of matter for electrodepositing a chromium alloy material which comprises a conductive aqueous solution containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, the ions of at least one alloying metal selected from the group consisting of from 0.6 to 2.5 g./l. of iron ions, from 0.1 to 1.0 g./l. of nickel ions, from 0.1 to 1.0 g./l.

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of cobalt ions, and containing additionally from .1 to 10 g./l. of sulfonated saccharin.

14. A composition of matter for electrodepositing a chromium-iron alloy material which comprises a conductive aqueous solution containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, from 0.6 to 2.5 g./l. of iron ions, and containing additionally from .1 to 10 g./l. of sulfonated saccharin.

15. A composition of matter for electrodepositing a chromium-nickel alloy material which comprises a conductive aqueous solution containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, from 0.1 to 1.0 g./l. of nickel ions, and containing additionally from .1 to 10 g./l. of sulfonated saccharin.

16. A composition of matter for electrodepositing a chromium-cobalt alloy material which comprises a conductive aqueous solution containing from 30 to 75 g./l. of trivalent chromium ions, 10 to 50 g./l. of alkali metal ions, from 0.1 to 1.0 g./l. of cobalt ions, and containing additionally from .1 to 10 g./l. of sulfonated saccharin.

References Cited in the file of this patent

UNITED STATES PATENTS

25	2,377,229	Harford	May 29, 1945
	2,655,471	Chester	Oct. 13, 1953
	2,704,273	Yoshida	Mar. 15, 1955
	2,766,196	Yoshida	Oct. 9, 1956

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,822,326

February 4, 1958

William H. Safranek

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 16, for "pridium" read -- pyridium --; column 8, line 12, for "Diamino pyridine" read -- Dimethylthiourea --.

Signed and sealed this 25th day of March 1958.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

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Commissioner of Patents