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2,990,343

CHROMIUM ALLOY PLATING

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This invention relates to coatings containing chromium. More particularly, it relates to a process and to an electrolyte for electrodepositing chromium alloys.

It is frequently desirable to provide a decorative coating for metal surfaces which can be buffed to a high luster, which will retain its hardness, and which will protect against corrosion. Conventional chromium plate usually has a bright surface only when it is deposited on a smooth bright metal but when the conventional chromium plate is deposited on a rough, dull base metal the plate is dull and rough, and is difficult to buff to a high luster. Also, conventional chromium plates will not retain hardness when heated and do not provide adequate protection against corrosion or high temperatures.

It has been found that suitable trivalent chromium salt baths can be used to electrodeposit chromium alloy plate with a high degree of success. In U.S. Patent 2,693,444, Snavelly et al., there is disclosed a chromium-alloy plating bath containing; chromium ammonium sulfate, ammonium sulfate, magnesium sulfate, ammonium hydroxide, sodium sulfite, salts of alloying metals, and water. Although the electroplates obtained from these baths retained their hardness at high temperatures, their coatings were hard to buff and did not always afford complete protection to the base metals in corrosive atmospheres.

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 prior-art electroplates.

Accordingly, one of the objects of this invention is to provide a smooth chromium-alloy coating which will easily buff to a mirrorlike appearance. Another object is to provide a chromium-alloy plate which will retain its hardness after heating to elevated temperatures. A further object is to provide a plate or coating for metals which is rustproof and relatively free from the customary cracking which exists in conventional chromium electrodeposits. Other objects and advantageous features will be apparent from the following specification and examples.

In general, the process of this invention relates to electrolyzing an aqueous bath containing trivalent chromium ions, ions capable of conducting an electric current and ions of alloying metals. Trivalent chromium ions are provided by trivalent chromium salts or compounds, such as chromium ammonium sulfate, chromium sulfate, basic chromium sulfate, chromium fluoborate, chromic chloride, chromium carbonate, chromic oxide, or chromium potassium sulfate. Supplementary salts, such as sodium or ammonium sulfate, sodium fluoborate, sodium chloride, or a mixture of such salts, are added to provide ions that improve the conductivity of the electrolyte. Ions of alloying metals may be added as metal salts or compounds, such as metal sulfates or metal fluoborates. A suitable electric current is passed through the solution, while maintaining it at a proper temperature and pH, for a sufficient length of time to deposit the coating to the desired thickness.

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

Example I

Chromium-iron deposits were obtained from the following aqueous solution:

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	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 $[(\text{NH}_4)_2\text{SO}_4]$	150
Ferrous ammonium sulfate $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$	13

The pH was maintained at from 1.8 to 2.3 by means of sulfuric acid. The cathode current density was from 180 to 240 amperes per square foot and the temperature of the bath was 120 to 140° F. A chromium-iron-alloy anode containing 85 percent chromium and 15 percent iron was used. The anode efficiency, based on trivalent chromium present, was 55 percent, while the cathode efficiency was 50 percent.

The composition of the coating was found to be about 87 percent chromium and 13 percent iron. It was found that the coating was easy to buff to a high luster and that it exhibits superior resistance to cracking.

The chromium-iron-alloy plate was also tested for hot hardness. The hardness at room temperature was 426 Vickers; when heated to 930° F., the hardness (at temperature) was found to be 402 Vickers, after being held at 930° F. for 21 hours, and, while still at temperature, the hardness was found to be 372 Vickers. The sample was then heated to 1300° F. where the hardness was found to be 203 Vickers, and, after being held at 1300° F. for 21 hours, the hardness was 189 Vickers. When the sample was allowed to return to room temperature, the hardness was found to be 391 Vickers.

Example II

This bath was similar to that used in Example I, except that 30 g./l. of ferrous ammonium sulfate were used. The cathode current density was 300 to 500 amperes per square foot, and the operating temperature was 130 to 140° F. Otherwise, operating conditions were the same as in Example II. Anode efficiency, based on trivalent chromium, was 55 percent, and cathode efficiency was 30 percent.

The composition of the resulting plate was 55 percent chromium and 45 percent iron. The plate could be easily buffed to a high luster.

Example III

Deposits consisting of 12 percent chromium and 88 percent iron were obtained from the following aqueous bath:

	G./l.
Basic chromium sulfate $[\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{O} \cdot 5\text{H}_2\text{O}]$..	300
Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$	150
Ferrous ammonium sulfate	
$[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$	130

The pH was maintained at 2.4 to 2.6 by means of adding sulfuric acid. The cathode current density was 300 amperes per square foot, the temperature of the solution was maintained at 125 to 130° F., the anode efficiency, based on trivalent chromium, was 55 percent, and the cathode efficiency 42 percent. A chromium-iron alloy anode was used.

Example IV

Deposits consisting of 89 percent chromium and 11 percent iron were obtained from the following aqueous solution:

	G./l.
Basic chromium sulfate	
$[\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{O} \cdot 5\text{H}_2\text{O}]$	425
Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$	50
Ferrous ammonium sulfate	
$[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$	18

The pH was maintained at 1.5 to 1.7 by means of small additions of sulfuric acid. The cathode current density was 250 amperes per square foot, the temperature of the

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solution was maintained at 120 to 130° F., the anode efficiency, based on trivalent chromium was 55 percent, and the cathode efficiency was 55 percent. A chromium-iron-alloy anode was used.

Example V

Deposits consisting of 94 percent chromium and 6 percent iron were obtained in the following aqueous solution:

	G./l.
Basic chromium sulfate [Cr ₂ (SO ₄) ₃ ·Na ₂ O·5H ₂ O]	450
Ammonium sulfate [(NH ₄) ₂ SO ₄]	25
Ferrous ammonium sulfate [Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O]	4.5

The pH was maintained at 1.6 to 1.9 by means of sulfuric acid. The cathode current density was maintained at 250 amperes per square foot and the temperature of the bath was 120 to 130° F. A chromium-iron-alloy anode containing 94 percent chromium and 6 percent iron was used. Anode efficiency, based on the trivalent chromium was 55 percent and the cathode efficiency 45 percent.

Example VI

Deposits consisting of about 95 percent chromium and 5 percent iron were obtained in the following aqueous solution:

	G./l.
Basic chromium sulfate [Cr ₂ (SO ₄) ₃ ·Na ₂ O·5H ₂ O]	225
Ammonium sulfate [(NH ₄) ₂ SO ₄]	40
Ferrous ammonium sulfate [Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O]	4

The pH was maintained at 1.6 to 1.8 by means of sulfuric acid. The cathode current density was 125 to 150 amperes per square foot, and the temperature of the bath was 140° F. A chromium-iron-alloy anode was used. Anode efficiency was 50 percent and cathode efficiency was 40 to 50 percent.

Example VII

Deposits containing 90 percent chromium and 10 percent iron were obtained in the following aqueous bath:

	G./l.
Basic chromium sulfate [Cr ₂ (SO ₄) ₃ ·Na ₂ O·5H ₂ O]	450
Ammonium sulfate [(NH ₄) ₂ SO ₄]	150
Ferrous ammonium sulfate [Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O]	13
Boric acid [H ₃ BO ₃]	45

The pH was maintained at 1.8 to 2.3 by means of sulfuric and boric acids. The cathode current density was 200 to 400 amperes per square foot and the temperature of the bath was 130 to 140° F. A chromium-iron-alloy anode was used. The anode efficiency, based on trivalent chromium, was 55 percent, and on the cathode 30 percent.

Example VIII

Deposits containing 95 percent chromium and 5 percent iron were obtained in the following aqueous solution:

	G./l.
Chromium ammonium sulfate [Cr(NH ₄)(SO ₄) ₂ ·12H ₂ O]	300
Ammonium sulfate [(NH ₄) ₂ SO ₄]	50
Ferrous ammonium sulfate [Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O]	4.5

The pH was adjusted to about 1.9 by adding ammonium hydroxide. The cathode current density was 100 amperes per square foot and the temperature was 130° F. Lead anodes in porous cups were used. The cathode efficiency based on the trivalent chromium was 59 percent.

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Example IX

Deposits containing 94 percent chromium and 6 percent iron were obtained in the following aqueous solution:

	G./l.
Chromium ammonium sulfate [Cr(NH ₄)(SO ₄) ₂ ·12H ₂ O]	300
Ammonium sulfate [(NH ₄) ₂ SO ₄]	150
Ferrous ammonium sulfate [Fe(NH ₄)(SO ₄) ₂ ·6H ₂ O]	4.5

The pH was adjusted to about 1.8 to 2.2 by adding ammonium hydroxide. The cathode current density was from 100 to 150 amperes per square foot and the temperature of the bath was 115 to 120° F. Iron-silicon-alloy anodes were used. Cathode efficiency, based on trivalent chromium was 35 percent.

This bath was operated for several months under the conditions cited, except that chromium-iron-alloy anodes containing 85% chromium and 15% iron were used. The chromium and iron concentrations were gradually increased from about 30 to 40 g./l. and from about 0.65 to about 1.2 g./l., due to the difference between the anode and cathode efficiencies, which were about 55 and 35 percent, respectively. As a result of these changes in chromium and iron concentrations, the chromium contents of the deposits decreased from about 95 to 85 percent. The iron content increased from about 5 to 15 percent. The pH was maintained at about 2.0 by adding a small amount of sulfuric acid as required. The reproduction of many good protective chromium-iron-alloy plates during this period served to demonstrate the constancy and uniformity of the deposition conditions.

Example X

Deposits containing 85 to 90 percent chromium and 10 to 15 percent iron were obtained in the following aqueous solution:

	G./l.
Chromium ammonium sulfate [Cr(NH ₄)(SO ₄) ₂ ·12H ₂ O]	350
Ammonium sulfate [(NH ₄) ₂ SO ₄]	150
Ferrous ammonium sulfate [Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O]	6

The pH was adjusted to about 1.9 by adding ammonium hydroxide. The cathode current density was 100 amperes per square foot and the temperature of the bath was 115° F. Platinum anodes were used. Cathode efficiency was 25 percent.

The alloy plates obtained in Example XI were found to have a Knoop hardness of 550 to 600. After holding the sample at 700° F. for two hours and cooling to room temperature, it was found the Knoop hardness had gone up to 600-650.

This bath was used for several months. Additions of chromium ammonium sulfate and ferrous ammonium sulfate were made as required to maintain the concentrations of chromium and ammonium in the ranges of 34 to 39 g./l. and 0.8 to 0.95 g./l., respectively. The pH was maintained in the range of 1.9 to 2.0 by adding ammonium hydroxide as required. Smooth plates, free of cracks, blisters, or other defects, were reproduced time after time on a variety of articles with different shapes. Cylindrical objects were agitated by rotating them on their central axis. Flat steel panels were generally moved back and forth with cathode-bar agitation. For best results, the edges of the flat panels were protected from excessive current by shielding them with nonconductive shields.

Example XI

Deposits containing 1 percent nickel and the balance

chromium were obtained in the following aqueous solution:

	G./l.
Chromium ammonium sulfate [Cr(NH ₄)(SO ₄) ₂ ·12H ₂ O] -----	300
Ammonium sulfate [(NH ₄) ₂ SO ₄] -----	150
Nickel sulfate [NiSO ₄ ·6H ₂ O] -----	1.5

The pH was adjusted to about 2.5 by adding ammonium hydroxide. The cathode current density was from 80 to 100 amperes per square foot and the temperature of the bath was 115° F. Platinum anodes were used. Cathode current efficiency was 43 percent (at a current density of 100 amperes per square foot).

Example XII

Deposits containing approximately 3 percent iron and the balance chromium were obtained in the following aqueous solution:

	G./l.
Chromic oxide (26% Cr ₂ O ₃) -----	180
Ammonium sulfate [(NH ₄) ₂ SO ₄] -----	116.5
Ferrous ammonium sulfate [Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O] --	4.5

The pH was adjusted to 1.9 by adding sulfuric acid and the solution was heated to 120° F. Smooth chromium-iron-alloy plate up to 0.0013-inch thick was obtained in 30 minutes with a current density in the range of 65 to 120 amperes per square foot

Example XIII

Deposits containing approximately 3 percent iron and the balance chromium were obtained in the following aqueous solution:

	G./l.
Chromic oxide (26%, Cr ₂ O ₃) -----	65
Chromium fluoborate [Cr(BF ₄) ₃] -----	60
Sodium fluoborate [NaBF ₄] -----	70
Ferrous fluoborate [Fe(BF ₄) ₂] -----	11

The pH of the bath was adjusted to 2.4 by adding fluoboric acid and the temperature was raised to 115° F. Smooth chromium-iron-alloy plate up to 0.0015-inch thick was obtained in 30 minutes with a current density of 400 amperes per square foot.

The chromium fluoborate of Example XIII was prepared by dissolving 1 part of electrolytic chromium in 12 parts of 43 percent fluoboric acid solution. The ferrous fluoborate was prepared by dissolving 1 part of iron powder in 10 parts of 43 percent fluoboric acid solution.

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

Heretofore, it has been necessary that no hexavalent chromium ions be present in a chromium alloy plating bath or, if present, special precautions had to be taken. The special precautions involved placing insoluble anodes within diaphragms or porous cups to separate chromium chromate formed by anodic oxidation of trivalent chromium at the lead anode from the solution surrounding the cathode. If porous cups or diaphragms were not used, oxidizing agents such as hydrogen peroxide had to be added to the bath to oxidize the hexavalent chromium ions to form perchromate ions, which were unstable and revert to trivalent chromium ions. However, in the improved bath and process of this invention, porous cups or diaphragms, or the addition of oxidizing agents are unnecessary when an iron-silicon-alloy anode containing about 15 percent silicon, or a platinum anode is used as the insoluble anode. Substantially little or no trivalent chromium is oxidized at the surface of the iron-silicon alloy or the platinum anodes. Thus, hexavalent chromium is not formed in excess, as it is when lead or lead-

alloy anodes are used without porous cups or diaphragms. Also, alloy anodes made of chromium and iron were used without porous cups that did not cause excessive amounts of hexavalent chromium to be formed at the anode surfaces. It has been found that generally when using chromium-iron anodes, if the anode current density is maintained at about from 25 to 75 amperes per square foot, the chromium in the bath remains in the trivalent state.

Chromium and chromium-alloy plates may be obtained from these baths while using a pH of from 1.0 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, chromic sulfate, and chromium fluoborate, 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 chromic oxide require acid additions to obtain the proper initial pH. Sulfuric acid is preferred. During operation of the baths, either those in which chromium ammonium sulfate or other trivalent chromium chemicals 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. For best results, the borate ion concentration should not exceed 45 g./l. 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.

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 agent, and oxidation products thereof, since an excess of the reducing agent is used to complete the reduction. Thus, plating 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 baths 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.

As has been stated, trivalent chromium ions can be supplied to the plating baths by the addition of trivalent chromium salts, such as chromium ammonium sulfate, chromium sulfate, basic chromium sulfate, chromium fluoborate, chromic chloride, chromium carbonate and chromium potassium sulfate. Other trivalent chromium compounds which are not salts, such as chromic oxide, also can be used as a source of trivalent chromium ions. The amount of trivalent chromium ions used in the bath is dependent on the current density at which the bath is operated and the chromium salt or compound added to the bath to provide chromium ions. Satisfactory results have been obtained with concentrations ranging from 20 grams per liter to saturation. However, lower concentrations of from 20 to 75 grams per liter have been found to be the most satisfactory. Good plates were obtained from a bath containing more than 70 grams per liter of trivalent chromium ions, using chrome alum salts, but when the bath cooled to 135° F., salt crystals precipitated. In general, smaller trivalent chromium ion concentrations will result in better "throwing power." When chromic chloride is added to the bath as a source of trivalent chromium ions, for best results, the chloride ion concentration should not be allowed to exceed 40 grams per liter. If chromic oxide is used as the source of trivalent chromium ions, additions of sulfuric acid are neces-

sary to adjust the pH and to provide sulfate ion concentration which, for best results, should be not less than 80 grams per liter. If chromium potassium sulfate is used, the potassium ion concentration of the bath should not exceed 150 grams per liter. When using chromium fluoborate baths, a sulfate ion concentration is not required.

The alloying constituents of the plating baths are added to the baths 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. In plating baths where chromium fluoborate is used as the source of trivalent chromium ions, the alloying metal preferably should be added as a metal fluoborate salt. For instance, if iron is the alloying element, it should be added as ferrous fluoborate; however, mixed sulfate and fluoborate salts may be used. The amount of alloying metal ions added to the bath is dependent on the composition of alloy plate desired. Alloy plates can be produced that are predominantly iron or nickel in composition; however, by confining the ferrous or ferric ion concentration to from 0.6 to 2.5 grams per liter, or the nickel ions to from 0.1 to 1.0 gram per liter, 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 iron, that is from .6 to 2.5 grams per liter.

Various ternary or even quaternary combinations of these metals can be electrodeposited in the form of adherent hard alloy plates. For example, a chromium-iron-nickel alloy or a 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 salt and trivalent chromium compounds to obtain ternary or quaternary alloy plates.

In practicing this invention, the proper concentration of the desired metal ammonium sulfate may also be achieved by adding ammonium sulfate and a suitable metal compound separately in correct proportions. Any soluble salt or metal oxide may be used which does not introduce undesired ions in the bath.

Alkali metal compounds are added to the bath to maintain good throwing power. The term "alkali metal compounds" is intended to include ammonium compounds. Ammonium sulfate, sodium sulfate, and sodium fluoborate have all proved to be satisfactory when used for this purpose, but other alkali metal compounds, such as sodium chloride and potassium sulfate may be used as well. I have found ammonium compounds to be the most effective for this purpose. The alkali metal compounds may be added separately or as mixtures. Additions of electrolytes are particularly effective when plating is done with a low-current density and low concentrations of trivalent chromium ions. Concentrations of electrolytes in the plating baths 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 without further additions of an electrolyte. For best results, the total alkali-metal ion concentration should be within the concentration range of

from 10 to 150 grams per liter. In baths where sulfate salts are employed, total sulfate ion concentration should be within the range of from 80 to 600 grams per liter, and in fluoborate baths total fluoborate ion concentration should not exceed 500 grams per liter. Chloride salts, such as sodium chloride, may be used to replace sulfate or fluoborate salts; however, chloride ion concentration should not exceed 40 grams per liter. It has been found that if too much of the electrolyte salts are used, the resulting plate will not buff easily.

Satisfactory plating has been obtained by using current densities of from 75 to 500 amperes per square foot. As has been shown, the proper current density is dependent on the concentration of the trivalent chromium salt or additions used. 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. For example, it has been found that the chromium alloy can be electrodeposited at approximately 0.001-inch per hour at 100 amperes per square foot, and 0.0075-inch per hour at 500 amperes per square foot.

In the operation of the plating baths of this invention the temperatures of the solutions should be, preferably, within the range of from 105° F. to 145° F. For best results the temperature of any individual bath being operated at an unchanging current density should not vary more than 5 degrees from the operating temperature selected.

It is commonly known in commercial electroplating processes that, as the metal or metals are electrodeposited out of the bath onto the cathode, they must be replaced at the same rate. In the case of alloy electrodeposition, the metals must be replaced not only at the same rate but also substantially in the same ratio. When the plating baths of this invention are used, this replacement may be made when using either insoluble or soluble anodes, as will hereinafter be described.

When insoluble anodes are used, the bath is not replenished in chromium or iron. As a result of continuous operation, the concentrations of the chromium and alloying elements will diminish proportionally with the time of electrodeposition. These metals are constantly replaced by additions of metal compounds, such as the trivalent chromium salts or compounds originally used, and their alloying salts or soluble metal oxides or hydrates. The use of metal hydrates has proved to be very satisfactory in the sulfate salt baths, in that excess sulfates do not build up in the bath. Due to the fact that chromium hydroxide is only slightly soluble in weak acid solutions, such as the plating baths, a special form of chromium hydrate, prepared as described in U.S. Patent No. 2,436,509, should be used. Chromium hydrate, as prepared by this method, is both pure and soluble.

When it is desired to operate the plating bath continuously and for long periods of time, the most satisfactory results are obtained by using chromium-alloy anodes. Heretofore, it has been necessary to add chlorides to maintain soluble anodes active and prevent excessive hexavalent chromium from forming as a result of passive anodes. In the present baths, it has been found that no such additives are necessary. The anodes remain active and no excessive hexavalent ions are formed.

The use of soluble chromium-alloy anodes simplifies the plating process in that the need to replenish the bath with trivalent chromium salts or compounds is reduced or, upon proper balancing of the bath and plating operation, may be completely eliminated. The baths disclosed in Examples I and VI were operated for more than 30 days each, with soluble chromium-iron-alloy anodes. After these long periods of operation, good plates were being reproduced without making any changes in the operating conditions.

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It will, of course, be understood that the various details of the process may be varied without departing from the principles of this invention. It is, therefore, not the purpose to limit the patent other than is necessitated by the scope of the appended claims.

What is claimed is:

1. The method of electrodepositing a chromium-alloy plate which comprises electrolyzing an aqueous bath consisting of a chromium salt providing from 20 to 75 grams per liter of trivalent chromium ions, an alkali metal salt providing from 10 to 150 grams per liter of alkali metal ions, and a salt of at least one alloying metal providing alloying metal ions of the group consisting of from .6 to 2.5 grams per liter of iron ions, .1 to 1.0 gram per liter of nickel ions, and .1 to 1.0 gram per liter of cobalt ions.

2. The method of electrodepositing a chromium-iron alloy plate which comprises electrolyzing an aqueous bath consisting of a chromium salt providing from 20 to 75 grams per liter of trivalent chromium ions, an alkali metal salt providing 10 to 150 grams per liter of alkali metal ions, and a salt of an alloying metal providing .6 to 2.5 grams per liter of iron ions.

3. The method of electrodepositing a chromium-nickel

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alloy plate which comprises electrolyzing an aqueous bath consisting of a chromium salt providing from 20 to 75 grams per liter of trivalent chromium ions, an alkali metal salt providing 10 to 150 grams per liter of alkali metal ions and a salt of an alloying metal providing .1 to 1.0 gram per liter of nickel ions.

4. The method of electrodepositing a chromium-cobalt alloy plate which comprises electrolyzing an aqueous bath consisting of a chromium salt providing from 20-75 grams per liter of trivalent chromium ions, an alkali metal salt providing 10 to 150 grams per liter of alkali metal ions and a salt of an alloying metal providing .6 to 2.5 grams per liter of cobalt ions.

References Cited in the file of this patent

UNITED STATES PATENTS

2,693,444 Snavely et al. ----- Nov. 2, 1944

OTHER REFERENCES

Chemical Abstracts, vol. 35, page 1323.

Fuseya et al.: Transactions Electrochemical Society, vol. 59 (1931), pp. 445-460.