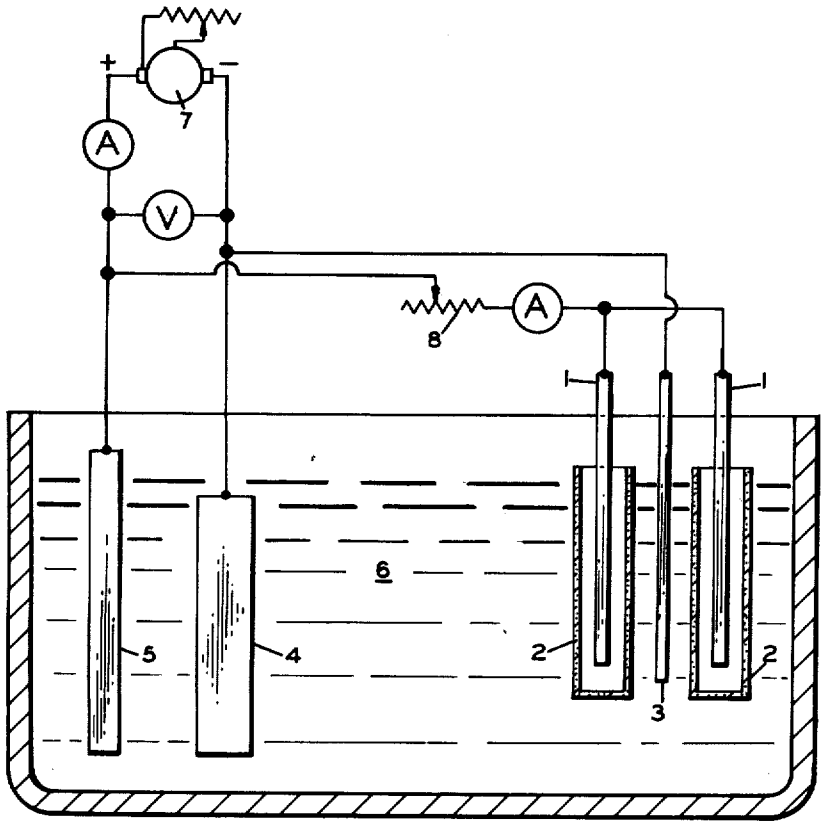
Nov. 19, 1963 W. H. SAFRANEK, JR., ETAL 3,111,464

ELECTRODEPOSITION OF CHROMIUM AND CHROMIUM ALLOYS

Filed Sept. 29, 1961



INVENTORS
WILLIAM H. SAFRANEK
JOHN G. BEACH
CHARLES L. FAUST
BY Gray, Mase, & Burnson
ATTORNEYS

United States Patent Office 3,111,464 Patented Nov. 19, 1963

3,111,464
ELECTRODEPOSITION OF CHROMIUM AND CHROMIUM ALLOYS

William H. Safranek, Jr., Worthington, and John G. Beach and Charles L. Faust, Columbus, Ohio, assignors, by mesne assignments, to The Battelle Development Corporation, Columbus, Ohio, a corporation of Delaware

Filed Sept. 29, 1961, Ser. No. 141,800
10 Claims. (Cl. 204—43)

This invention relates to chromium and chromium-alloy coatings. More particularly, it relates to a method and apparatus for electrodepositing chromium coatings which will retain hot hardness, and to the conditions for producing the coatings.

The use of chromium plating has been extended to fields other than that of decorative plating. Engineering applications utilize the very hard and wear-resistant properties of chromium plate. In chromium plating using the conventional hexavalent chromic acid (CrO_3) containing a catalyst such as sulfate, fluoride, fluosilicate, or other materials known in the art, the cathode current efficiencies are relatively low, 10 to 20 percent, based on the hexavalent chromium ion. Chromium plating in trivalent chromium baths (U.S. Patents 2,693,644 and 2,927,066) provides means of utilizing higher cathode current efficiencies; for example, 20 to 30 percent current efficiency based on trivalent chromium, or 40 to 60 percent current efficiency based on hexavalent chromium.

Chromium, although hard in the as-plated form, softens when heated above 900° F. Chromium as plated from the conventional chromic acid bath had a hardness of 800 KHN, but after heating at 1100° F., its hardness was only 300 KHN. This softening precludes the advantage of hardness for chromium plates when used at elevated temperatures. Chromium plates containing iron, however, retain hardness at elevated temperatures much better than does unalloyed chromium. Chromium-iron alloys containing 3 to 15 percent iron, as plated from the trivalent chromium bath, had hardnesses of 600 to 700 Knoop hardness numbers (KHN) and, after heating to 1100° F., retained 600 to 700 KHN. After heating at 1800° F., the hardness decreased to 400 KHN.

In the plating of chromium and chromium alloys from trivalent-chromium baths, difficulties often are encountered because the baths tend to become oxidized to hexavalent chromium baths, with a resultant loss of plating efficiency. Small amounts of hexavalent chromium in the trivalent chromium bath also cause inferior chromium plates. Chromium-iron alloy plates are produced in trivalent chromium baths containing ferrous iron. The ferrous iron is oxidized to the ferric state by hexavalent chromium or by anodic oxygen during electrolysis of the chromium-iron bath. The presence of ferric iron results in inferior chromium-iron alloy deposits.

The present invention overcomes the difficulties mentioned above and assures reliable plating at high efficiency by maintaining the trivalent chromium and chromium-iron alloy plating bath in the reduced state of Cr^{+2}, Cr^{+3}, and Fe^{+2} by the presence of the divalent chromium ion. The Cr^{+2} in the bath prevents any accumulation of Cr^{+6} and Fe^{+3}. Maintenance and control of the divalent chromium ion is a primary feature of this invention. By control of the divalent chromium concentration in the alloy plating

bath, reproducible chromium-iron alloy plates are deposited consistently at high cathode current efficiencies. This invention provides a means of producing chromium-iron alloy plates containing controlled amounts of iron up to about 15 percent, the balance chromium. It also provides a method of rapidly depositing a hot-hard chromium-containing coating, a thick chromium-containing coating that is free of the customary crack patterns. Other advantageous features of this invention will become apparent from the following description and examples. In general, this invention involves making an article to be plated the cathode in an electrolytic bath, a typical bath comprising a mixture of chromium ammonium sulfate, ferrous ammonium sulfate or ferrous sulfate, sulfamic acid, ammonium sulfate, and a predetermined concentration of divalent chromium ion. A suitable current is passed through the solution for a sufficient length of time to deposit the coating to the desired thickness on the cathode.

In the drawing, the FIGURE is a vertical sectional view, largely schematic, of typical apparatus according to the present invention.

A preferred method for maintaining and controlling the divalent chromium ion in the plating bath involves electrolysis using an auxiliary titanium cathode and auxiliary titanium anodes. The auxiliary anodes are coated with or coupled to platinum and are contained in porous cups. The plating bath is electrolyzed at a sufficient current to produce the desired divalent chromium ion concentration. The current density is maintained below that for the deposition of significant amounts of chromium or iron on the titanium auxiliary cathode. The titanium cathode, plated with hydrogen, provides a titanium hydride surface. The deposited hydrogen and the decomposition of the titanium hydride reduce Cr^{+3} to Cr^{+2}. The Cr^{+2} in turn reduces Fe^{+3} to Fe^{+2} and Cr^{+6} to Cr^{+3}.

The titanium-platinum auxiliary anodes are contained in porous cups with an anolyte comprising ammonium sulfate acidified to a pH of about 1 with sulfuric acid. With this anolyte, oxygen is liberated on the anode surface. Any chromium or iron ions from the catholyte that diffuse through the cups into the anolyte are oxidized to chromic acid or ferric iron, but are largely retained in the anolyte by virtue of the porous cups surrounding the anodes. Any chromic acid or ferric iron that diffuses back into the catholyte is reduced by the divalent chromium.

The chromium concentration in the bath is maintained by anodic dissolution of chromium metal. The chromium metal dissolves essentially in the hexavalent chromium condition and is reduced to trivalent chromium by the chromous ion present in the bath, $Cr^{+6}+3Cr^{+2}\rightarrow 4Cr^{+3}$. The chromium metal to be added to the bath is supported on a titanium metal tray, which is connected as the anode. Sufficient current is passed through the electrolyte to dissolve the chromium at such a rate that the Cr^{+6} is reduced to Cr^{+3} by the available Cr^{+2}, and excess Cr^{+6} in the electrolyte is avoided.

The iron concentration in the bath is maintained by anodic dissolution of iron metal similarly to the chromium metal dissolution.

We have found that divalent chromium concentration in the range of about 0.5 to 5 g./l. is necessary for chromium and chromium-iron alloy plating with improved cathode efficiency disclosed herein, and about 2.2 to 4 g./l. is optimum. During operation of the trivalent

chromium salt plating bath, soluble chromium anodes dissolve to introduce hexavalent chromium (CR^{+6}) into the bath, or with insoluble anodes the trivalent chromium (Cr^{+3}) is oxidized to hexavalent form. For most efficient operation the concentration of hexavalent form, Cr^{+6}, must be zero. Also, iron anodes dissolve in ferric (Fe^{+3}) state or the ferrous iron in the bath is oxidized to ferric iron whereas the ferrous (Fe^{+2}) state is desired. Thus, some means is needed for keeping the bath in the oxidation state of no hexavalent chromium and all divalent (ferrous) iron. This we have found can be assured only by having enough divalent chromium (Cr^{+2}) in the bath at all times that it can instantaneously react with any hexavalent chromium (Cr^{+6}) and ferric iron (Fe^{+3}) as they leave the vicinity of the anode and before the ions of these two metals can reach the deposition region of the cathode surface. By providing Cr^{+2} in the plating bath, the Cr^{+6} and the Fe^{+3} are reduced to Cr^{+3} and Fe^{+2}, respectively, without complete destruction of all the Cr^{+2}.

The reservoir of Cr^{+2} and Fe^{+2} in the plating bath may be provided and maintained by employing an auxiliary electrolysis circuit in the plating tank, as shown in the drawing. A pair of auxiliary anodes **1** are placed in cups **2** made of alundum or other porous inert material. The cups **2** retain the products of anodic oxidation, while an auxiliary cathode **3** reduces Cr^{+3} to Cr^{+2} at a cathode potential too low to significantly electrodeposit metal, say about 2 volts. By confining the auixiliary anodes **1** within the special compartments **2**, anodic oxidation of the Cr^{+2} is minimized or prevented so that enough Cr^{+2} is generated to offset formation of Fe^{+3} and Cr^{+6} at the main plating anodes. By this effective means, the plating bath is maintained in the desired reduced state wherein the dissolved chromium is maintained in the Cr^{+3} and Cr^{+2} conditions and the dissolved iron is maintained in the Fe^{+2} condition.

The auxiliary anodes **1** can be made of platinum, platinum-coated titanium, platinum-coated zirconium, platinum-coated tantalum or other metals or combination of conductive metals that do not dissolve in the anolyte.

Titanium, zirconium, chromium, and other metals that readly form surface hydrides with hydrogen when electrolyzed as a cathode, are preferred for the auxiliary cathode **3**. Although iron, steel, brass, copper, and similar metals can be used as the auxiliary cathode **3**, these metals are not as effective as metals such as titanium that readily form surface hydrides.

The principal anode **5** can be insoluble, soluble, or a combination of insoluble and soluble anodes in the ratio needed to maintain the metal ion concentration in the bath. Insoluble anodes can be made of platinum, platinum-coated titanium, and other conductive metal or combinations of metals that do not dissolve anodically in the bath. Soluble anodes can be made of chromium, iron, or chromium-iron alloys.

Good results for electrodepositing chromium iron alloy were obtained when the current density was 80 to 500 amperes per square foot on the main cathode **4**, the work piece to be plated. The temperature of the electrolyte **6** was 100 to 130° F.; the pH was 1.8 to 2.2; and the current density on the principal anode **5** was about 10 to 500 amperes per square foot. An adjustable direct current generator **7** supplied both the main electrodes **4**, **5** and the auxiliary electrodes **1**, **3**. A series rheostat **8** was used to reduce and control the voltage applied to the auxiliary electrodes **1**, **3**. The current to the auxiliary anodes **1** and the auxiliary cathode **3** was about 25 to 75 percent of the plating current; the auxiliary cathode current density being about 10 to 50 amperes per square foot, and anode current density being about 10 to 500 amperes per square foot.

Higher temperature, lower pH, and lower current density tended to reduce current efficiency. Higher pH and higher current density tended to cause faulty electroplates. Little to mild agitation on the cathode was beneficial to the quality of the chromium-iron alloy plate. Too much agitation caused faulty or no electroplate. Agitation of the bath is necessary to promote reduction of oxidized metal ions with the divalent chromium.

The following examples further illustrate the invention.

Example I

An aqueous bath of the following composition was prepared:

Chromium ammonium sulfate, $Cr_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	g./l.	365
Ammonium sulfate, $(NH_4)_2SO_4$	do	100
Sulfamic acid, NH_2SO_3H	do	50
Ammonium hydroxide 29 percent NH_4OH	ml.	80
Ferrous ammonium sulfate $(FeSO_4 \cdot NH_4)_2SO_4 \cdot 6H_2O$	g./l.	6.3
pH with H_2SO_4 or NH_4OH		2.0±0.2

The first three salts were dissolved in the above order in hot distilled water. The solution temperature was maintained at 160° F. or higher for one hour or more to convert the violet form of chromium ammonium alum to the green form of a complex containing monacid sulfate. The solution was cooled to about 115° F.±5° F. and the pH was adjusted to 2.0±0.2 by additions of ammonium hydroxide. The iron salt was dissolved.

The plating bath was electrolyzed using a titanium sheet auxiliary cathode and platinum-titanium auxiliary anodes contained in porous cups (fine-grain extraction thimble-alundum mixture RA–84, Norton Company, for retention of materials with particle size 0.1 micron or greater) at a current density of 15 amperes per square foot, with enough cathode area to permit 0.5 ampere per gallon for 24 hours. This reducing electrolysis produced a divalent chromium concentration in the bath between 2.2 and 4 g./l. The bath contained no hexavalent chromium and no ferric iron. The steel cathode plated in this reduced bath at 115 amperes per square foot for 60 minutes showed a cathode current efficiency of 34 to 37 percent based on Cr^{+3} and Fe^{+2}. The deposit contained about 95 percent chromium and 5 percent iron. The hardness of the chromium-iron alloy deposit was 700 KHN.

Example II

The same steps were followed as in Example I except that the electrolysis of the bath with auxiliary electrodes was omitted. The deposit did not adhere satisfactorily in many areas and was generally inferior and unsatisfactory.

To summarize, the present invention includes, in a method of electroplating of chromium and chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, in a trivalent chromium-type plating bath comprising about

200 to 700 grams per liter of chromium ammonium sulfate, about
2 to 15 grams per liter of a material of the group consisting of ferrous ammonium sulfate and ferrous sulfate, about
0 to 75 grams per liter of sulfamic acid, and about
50 to 150 grams per liter of ammonium sulfate, the bath having a pH of about
1.8 to 2.2,

the improvement that comprises providing and maintaining a reservoir of about 0.5 to 5 (preferably about 2.2 to 4) grams per liter of divalent chromium in the bath. This is accomplished by electrolyzing the bath with an auxiliary cathode preferably comprising titanium, zirconium, chromium, or other metals that readily form surface hydrides when electrolyzed as a cathode, at least one auxiliary anode preferably comprising platinum, or platinum-coated materials such as titanium, zirconium,

and tantalum, or other conductive metallic materials that do not dissolve in the anolyte, an anolyte comprising ammonium sulfate acidified to a pH of about 0.1 to 2.2 surrounding each auxiliary anode, and a porous member between the anolyte and the plating bath, maintaining the bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent condition and to maintain any dissolved iron thereon in the divalent condition.

In a preferred embodiment, the invention comprises a method of electroplating chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, on a conductive cathode in a trivalent chromium-type plating bath comprising about

200 to 700 grams per liter of chromium ammonium sulfate, about
2 to 15 grams per liter of a material of the group consisting of ferrous ammonium sulfate and ferrous sulfate, about
0 to 75 grams per liter of sulfamic acid, and about
50 to 150 grams per liter of ammonium sulfate, the bath having a pH of about
1.8 to 2.2,

at a cathode current density of about 80 to 500 amperes per square foot and an anode current density of about 10 to 500 amperes per square foot, maintaining the temperature of the bath at about 100 to 130° F., that comprises electrolyzing the bath with an auxiliary cathode, preferably having a metal hydride surface, at least one auxiliary anode, preferably having platinum on the surface thereof, an anolyte, preferably comprising ammonium sulfate acidified to a pH of about 0.1 to 2.2, surrounding each auxiliary anode, and a porous member between the anolyte and the plating bath, preferably at an auxiliary cathode current density of about 10 to 50 amperes per square foot and an auxiliary anode current density of about 10 to 500 amperes per square foot, with the current to the auxiliary electrodes of about 25 to 75 percent of the current to the plating electrodes.

In terms of chromium and iron ion concentrations, the invention comprises a method of electroplating chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, that comprises electrolyzing an aqueous solution consisting essentially of about 20 to 75 grams per liter of trivalent chromium, about 0.5 to 5 (preferably about 2.2 to 4) grams per liter of divalent chromium, about 0.5 to 5 (preferably about 0.5 to 3) grams per liter of ferrous iron, about 50 to 150 grams per liter of ammonium sulfate, and about 0 to 75 grams per liter of sulfamic acid, the solution having a pH of about 1.8 to 2.2. In still different terms, the invention comprises a method of maintaining a trivalent chromium-type plating bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent conditions and to maintain any dissolved iron therein in the divalent condition that comprises electrolyzing the bath with an auxiliary cathode and at least one auxiliary anode, an anolyte comprising ammonium sulfate acidified to a pH of about 0.1 to 2.2 surrounding each auxiliary anode, and a porous member between the anolyte and the plating bath, at an auxiliary cathode current density of about 10 to 50 amperes per square foot and an auxiliary anode current density of about 10 to 500 amperes per square foot.

What is claimed is:

1. In a method of electroplating of chromium and chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, in a trivalent chromium-type plating bath comprising about

200 to 700 grams per liter of chromium ammonium sulfate, about
2 to 15 grams per liter of a material of the group consisting of ferrous ammonium sulfate and ferrous sulfate, about

0 to 75 grams per liter of sulfamic acid, and about
50 to 150 grams per liter of ammonium sulfate, said bath having a pH of about
1.8 to 2.2,

the improvement that comprises providing and maintaining a reservoir of about 0.5 to 5 grams per liter of divalent chromium in said bath, by electrolyzing said bath with an auxiliary cathode, at least one auxiliary anode, an anolyte surrounding each said auxiliary anode, and a porous member between said anolyte and said plating bath, at a current that maintains said bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent condition and to maintain any dissolved iron therein in the divalent condition, the current density being insufficient to cause substantial electrodeposition of metal upon said auxiliary cathode.

2. In a method of electroplating of chromium and chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, in a trivalent chromium-type plating bath comprising about

200 to 700 grams per liter of chromium ammonium sulfate, about
2 to 15 grams per liter of a material of the group consisting of ferrous ammonium sulfate and ferrous sulfate, about
0 to 75 grams per liter of sulfamic acid, and about
50 to 150 grams per liter of ammonium sulfate, said bath having a pH of about
1.8 to 2.2,

the improvement that comprises providing and maintaining a reservoir of about 0.5 to 5 grams per liter of divalent chromium in said bath, by electrolyzing said bath with an auxiliary cathode having a metal hydride surface, at least one auxiliary anode having platinum on the surface thereof, an anolyte comprising ammonium sulfate acidified to a pH of about 0.1 to 2.2 surrounding each said auxiliary anode, and a porous member between said anolyte and said plating bath, at a current that maintains said bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent condition and to maintain any dissolved iron therein in the divalent condition, the current density being insufficient to cause substantial electrodeposition of metal upon said auxiliary cathode.

3. In a method of electroplating of chromium and chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, in a trivalent chromium-type plating bath comprising about

200 to 700 grams per liter of chromium ammonium sulfate, about
2 to 15 grams per liter of a material of the group consisting of ferrous ammonium sulfate and ferrous sulfate, about
0 to 75 grams per liter of sulfamic acid, and about
50 to 150 grams per liter of ammonium sulfate, said bath having a pH of about
1.8 to 2.2,

the improvement that comprises providing and maintaining a reservoir of about 0.5 to 5 grams per liter of divalent chromium in said bath, by electrolyzing said bath with an auxiliary cathode comprising a material of the group consisting of titanium, zirconium, and chromium, having a hydride surface, at least one auxiliary anode comprising a material of the group consisting of platinum, titanium, zirconium, and tantalum, having platinum on the surface thereof, an anolyte comprising ammonium sulfate acidified to a pH of about 0.1 to 2.2 surrounding each said auxiliary anode, and a porous member between said anolyte and said plating bath, at a current that maintains said bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent condition and to main-

tain any dissolved iron therein in the divalent condition, the current density being insufficient to cause substantial electrodeposition of metal upon said auxiliary cathode.

4. A method of electroplating chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, on a conductive cathode in a trivalent chromium-type plating bath comprising about

200 to 700 grams per liter of chromium ammonium sulfate, about
2 to 15 grams per liter of a material of the group consisting of ferrous ammonium sulfate and ferrous sulfate, about
0 to 75 grams per liter of sulfamic acid, and about
50 to 150 grams per liter of ammonium sulfate, said bath having a pH of about
1.8 to 2.2,

at a cathode current density of about 80 to 500 amperes per square foot and an anode current density of about 10 to 500 amperes per square foot, that comprises electrolyzing said bath with an auxiliary cathode, at least one auxiliary anode, an anolyte surrounding each said auxiliary anode, and a porous member between said anolyte and said plating bath, at an auxiliary cathode current density of about 10 to 50 amperes per square foot and an auxiliary anode current density of about 10 to 500 amperes per square foot, with the current to said auxiliary electrodes of about 25 to 75 percent of the current to the plating electrodes.

5. A method of electroplating chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, on a conductive cathode in a trivalent chromium-type plating bath comprising about

200 to 700 grams per liter of chromium ammonium sulfate, about
2 to 15 grams per liter of a material of the group consisting of ferrous ammonium sulfate and ferrous sulfate, about
0 to 75 grams per liter of sulfamic acid, and about
50 to 150 grams per liter of ammonium sulfate, said bath having a pH of about
1.8 to 2.2,

at a cathode current density of about 80 to 500 amperes per square foot and an anode current density of about 10 to 500 amperes per square foot, maintaining the temperature of said bath at about 100 to 130° F., that comprises electrolyzing said bath with an auxiliary cathode comprising a material of the group consisting of titanium, zirconium, and chromium having a hydride surface, at least one auxiliary anode comprising a material of the group consisting of platinum, titanium, zirconium, and tantalum, having platinum on the surface thereof, an anolyte comprising ammonium sulfate acidified to a pH of about 0.1 to 2.2 surrounding each said auxiliary anode, and a porous member between said anolyte and said plating bath, at an auxiliary cathode current density of about 10 to 50 amperes per square foot and an auxiliary anode current density of about 10 to 500 amperes per square foot, with the current to said auxiliary electrodes of about 25 to 75 percent of the current to the plating electrodes.

6. A method of maintaining a trivalent chromium-type plating bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent conditions and to maintain any dissolved iron therein in the divalent condition, that comprises electrolyzing said bath with an auxiliary cathode, at least one auxiliary anode, an anolyte surrounding each said auxiliary anode, and a porous member between said anolyte and said plating bath, at a current sufficient to provide said reduced state and a current density insufficient to cause substantial electrodeposition of metal upon said auxiliary cathode.

7. A method of maintaining a trivalent chromium-type plating bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent conditions and to maintain any dissolved iron therein in the divalent condition, that comprises electrolyzing said bath with an auxiliary cathode comprising a material of the group consisting of titanium, zirconium, and chromium, having a hydride surface, at least one auxiliary anode comprising a material of the group consisting of platinum, titanium, zirconium, and tantalum, having platinum on the surface thereof, an anolyte comprising ammonium sulfate acidified to a pH of about 0.1 to 2.2 surrounding each said auxiliary anode, and a porous member between said anolyte and said plating bath, at an auxiliary cathode current density of about 10 to 50 amperes per square foot and an auxiliary anode current density of about 10 to 500 amperes per square foot.

8. In a method of electroplating of chromium and chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, in a trivalent chromium-type plating bath comprising about

200 to 700 grams per liter of chromium ammonium sulfate, about
2 to 15 grams per liter of a material of the group consisting of ferrous ammonium sulfate and ferrous sulfate, about
0 to 75 grams per liter of sulfamic acid, and about
50 to 150 grams per liter of ammonium sulfate, said bath having a pH of about
1.8 to 2.2,

the improvement that comprises providing and maintaining a reservoir of about 2.2 to 4 grams per liter of divalent chromium in said bath, by electrolyzing said bath with an auxiliary cathode, at least one auxiliary anode, an anolyte surrounding each said auxiliary anode, and a porous member between said anolyte and said plating bath, at a current that maintains said bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent condition and to maintain any dissolved iron therein in the divalent condition, the current density being sufficient to cause substantial electrodeposition of metal upon said auxiliary cathode.

9. A method of electroplating chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, that comprises electrolyzing an aqueous solution consisting essentially of about

20 to 75 grams per liter of trivalent chromium, about
0.5 to 5 grams per liter of divalent chromium, about
0.5 to 5 grams per liter of ferrous iron, about
50 to 150 grams per liter of ammonium sulfate, and about
0 to 75 grams per liter of sulfamic acid, said solution having a pH of about
1.8 to 2.2,

said divalent chromium being provided and maintained by electrolyzing said solution with an auxiliary cathode, at least one auxiliary anode, an anolyte surrounding each said auxiliary anode, and a porous member between said anolyte and said aqueous solution, at a current that maintains said bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent condition and to maintain any dissolved iron therein in the divalent condition, the current density being insufficient to cause substantial electrodeposition of metal upon said auxiliary cathode.

10. A method of electroplating chromium-iron alloys containing up to about 15 percent iron, the balance essentially chromium, that comprises electrolyzing an aqueous solution consisting essentially of about

20 to 75 grams per liter of trivalent chromium, about
2.2 to 4 grams per liter of divalent chromium, about
0.5 to 3 grams per liter of ferrous iron, about
50 to 150 grams per liter of ammonium sulfate, and about
0 to 75 grams per liter of sulfamic acid, said solution having a pH of about
1.8 to 2.2,

said divalent chromium being provided and maintained by electrolyzing said solution with an auxiliary cathode, at least one auxiliary anode, an anolyte surrounding each said auxiliary anode, and a porous member between said anolyte and said aqueous solution, at a current that maintains said bath in a sufficiently reduced state to maintain the dissolved chromium therein in the trivalent and divalent condition and to maintain any dissolved iron therein in the divalent condition, the current density being insufficient to cause substantial electrodeposition of metal upon said auxiliary cathode.

References Cited in the file of this patent

UNITED STATES PATENTS

1,414,423	Langer	May 2, 1922
1,922,853	Kissel	Aug. 15, 1933
2,316,917	Wallace et al.	Apr. 20, 1943
2,990,343	Safranek	June 27, 1961