United States Patent Office 3,282,812 Patented Nov. 1, 1966

3,282,812

ELECTRODEPOSITION OF CHROMIUM

Henry Brown, Huntington Woods, and Edward A. Romanowski, Troy, Mich., assignors to The Udylite Corporation, Warren, Mich., a corporation of Delaware

No Drawing. Filed Feb. 20, 1964, Ser. No. 346,116
12 Claims. (Cl. 204—51)

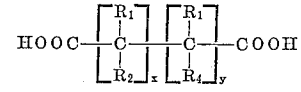
This invention relates to improvements in the electrodeposition of chromium from aqueous acidic hexavalent chromium solutions. More particularly it relates to the electrodeposition of chromium plate of improved covering power, which is accomplished by the use of new stable organic additives to acidic hexavalent chromium electroplating baths. These new organic additives to acidic hexavalent chromium plating baths function as cooperating activators with minimum concentrations of catalyst ion (the inorganic sulfate anion) to make possible chromium plate of extremely good covering power without complicating the operation of the chromium plating bath.

In order to electrodeposit chromium from acidic hexavalent chromium solutions, that is, chromic acid solutions, it was early established that it was necessary to have present in the bath small concentrations of certain anions such as the sulfate ion, and included with the sulfate ion, fluoride ions and other ions were also named as effective catalyst anions. However, many anions were termed catalyst anions that merely aided the effect of low concentrations of sulfate ions. It really appears that the sulfate anion is the only true "catalyst" anion and that the other mentioned anions have auxiliary effects.

The standard or conventional chromium bath employing only the sulfate anion as catalyst and used for plating on nickel, ferrous surfaces, yellow brass, or copper has been the 100 to 1 ratio of chromic acid anhydride (CrO_3) to sulfate ion. Thus in a 200 gram/liter chromic acid bath, 2 grams/liter of sulfate ion would be used, and in a 400 gram/liter chromic acid bath, 4 grams/liter of sulfate ion would be used. If one uses instead a ratio of 200 to 1 of CrO_3 to SO_4 and plates on top of nickel, copper, yellow brass or steel, only an irridescent (rainbow) non-metallic chromium chromate film is obtained instead of chromium plate if "dead" entry into the chromium plating bath is used. Furthermore, if chromium plating is attempted on top of a freshly plated bright nickel surface, from an aqueous solution containing, for example, 340 grams/liter (45 oz./gal.) of chromic acid and saturated with strontium sulfate at, for example, about 50–52° C. (approx. 125° F.) which yields a ratio of chromic acid to dissolved sulfate ion of about 160 to 1, and using "dead" entry into this chromic acid bath (that is, the direct plating current is turned on only after the nickel plated panel is immersed in the bath), no chromium plate is obtained on the nickel surface, only a non-metallic iridescent film of a basic chromic chromate results. However, if live entry is used, that is, the electrical connection is made before the nickel plated panel is immersed into the chromic acid bath, and the plating thus is started just as the panel or work goes into the bath, then a chromium plate is obtained on the nickel. With white brass plate (80% zinc and 20% copper alloy plate), even with dead entry into the chromium plating bath of 200 to 1 ratio of chromic acid to sulfate chromium plate is obtained on top of the white brass plate. It is believed that the white brass surface is less passive than the nickel surface and that the sulfate ion functions in part as "catalyst" and in part as an activator of passive surfaces such as nickel surfaces. The longer the nickel surface is allowed to stay in contact with the chromic acid solution with no current on, and the more

concentrated the chromic acid, the poorer will be the chromium coverage. If the sulfate ion is increased much beyond the 100 to 1 ratio, for example, to 50 to 1 ratio of chromic acid to sulfate, then the chromium coverage gets poorer and poorer and finally with a large excess of sulfate ion no chromium plate is obtained, and merely trivalent chromium is formed at the cathode.

It has now been found that by the use of certain aliphatic dicarboxylic acids characterized by Formula A below, in conjunction with low concentrations of the catalyst sulfate anion, it is possible to obtain extremely good chromium coverage with chromic acid baths of about 150 to 1, 200 to 1, and 300 to 1 ratios of chromic acid to sulfate. Even 400 to 1 ratios of chromic acid to sulfate are helped by the dicarboxylic acids of Formula A.



(A)

where $x=0$, 1 or 2 and $y=1$ or 2
when $x=0$, and $y=1$; R_3 and R_4=F, Cl or Br
when $x=1$, and $y=1$; R_1 and R_3=F or Cl and R_2=F, Cl, or Br and R_4= F, Cl, Br or H
when $x+y=3$ or 4; R_1, R_2, R_3 and R_4=F only or F plus Cl with fluorine atoms equal in number or predominating the chlorine atoms.

The preferred compounds represented by Formula A are tetrachloro succinic acid (where $x=1$ and $y=1$ and R_1, R_2, R_3 and R_4 are chloro groups), tetrafluoro succinic acid, and hexafluoro glutaric acid. These last two perfluoro dicarboxylic acids are extremely stable to the powerful oxidation conditions existing at the lead and lead alloy anodes during electrolysis. The tetrachloro succinic acid is very resistant to oxidation by the chromic acid, and though not perfectly stable to the anodic oxidation, it is sufficiently stable and is practical to use because it is not too expensive to prepare. It can be made from tetrachloro butane-1,4-diol. This tetrachloro alcohol can be added as such to the chromic acid baths where it is rapidly oxidized to tetrachloro succinic acid, or it can be pre-oxidized before adding it to the chromium plating bath. Perfluoro adipic acid (octafluoro adipic acid) though it is extremely stable in the chromic acid baths is not quite as effective an activator as the smaller chain dicarboxylic acids, prefluoro succinic acid or perfluoro glutaric acid or tetrachloro succinic acid or dichloro difluoro succinic acid or dichloro dibromo succinic acid. The smallest of the halogen substituted dicarboxylic acids, that is the halogen substituted malonic acids tend to decarboxylate especially when concentrated and present in warm baths. Thus, the preferred Formula A dicarboxylic acids, as mentioned, are the tetrafluoro and tetrachloro succinic acids and hexafluoro glutaric acid, and perfluoro adipic acid, with the first two optimum.

The Formula A dicarboxylic acids without the sulfate anion do not make possible the electrodeposition of chromium from pure chromic acid solutions. However, in conjunction with small concentrations of sulfate anion they act as uncritical "activators," that is, the sulfate anion is needed but only in optimum concentration for its "catalytic" effect and not for any special activating effect.

It is not new to use carboxylic acids in acidic hexavalent chromium plating solutions, however, such carboxylic acids as acetic acid (or acetates) strongly attack the lead and lead alloy anodes that are used in chromic acid plating baths, and these anodes during use are corroded away at a rapid rate. This is also true for chloro acetic acids and trifluoro acetic acid. Du Rose in U.S. 2,784,153 (March 5, 1957) has found that the presence of cobalt

ions in the chromic acid bath decreases the attack by the acetates, however, the formula A dicarboxylic acids do not corrode the lead and lead alloy anodes nearly as fast as acetate ions or acetic acid, including mono-, di- and trichloroacetic acids (Murray, U.S. Patent 2,279,830, issued April 14, 1942), and trifluoroacetic acid, and this improvement represents a very important and unexpected advance in the art. The corrosive attack on the lead and lead alloy anodes by the formula A dicarboxylic acids is no greater than that which occurs in the widely used chromium plating baths employing sulfate plus fluosilicate "catalyst" ions. Acetic acid, and the mono-, di- and trichloroacetic acids and trifluoroacetic used in the same concentrations in the chromium plating bath as the formula A dicarboxylic acids attack the lead and lead alloy anodes at least five times faster.

Dicarboxylic acids such as tartaric, and phthalic acids are rapidly oxidized away by the chromic acid bath especially during electrolysis, and for this reason they are difficult to control, and the baths can accumulate excessive concentrations of trivalent chromium which is detrimental to the best operation of the baths. Also, certain carboxylic acids such as perfluoro n-hexanoic and perfluoro n-octanoic acid cause rather thick unsightly yellowish-brown films of basic chromium chromate in the low current density areas.

It is necessary to use lead or lead alloy anodes for most of the anode area in the acidic hexavalent chromium plating baths in order to efficiently re-oxidize the trivalent chromium ions formed at the cathode during the elertrodeposition of the chromium metal. If most of this this trivalent chromium is not re-oxidized, the chromium bath will become almost inoperative. The powerful oxidizing agent, lead dioxide, forms on the anodes during electrolysis, and this oxidizing agent re-oxidizes the trivalent chromium to the hexavalent form but does not oxidize the perfluoro succinic, perfluoro glutaric and the perfluoro adipic acid, and only slowly oxidizes away the tetrachloro succinic acid.

The acidic hexavalent chromium plating baths may be made up from straight chromic acid anhydride or chromic acid, and from mixtures with dichromates, chromates and polychromates. It is generally preferred to use straight chromic acid or chromic acid anhydride. The source of the sulfate ion may be sulfuric acid or one of its soluble salts, or from strontium sulfate in saturation concentrations, with or without added strontium ions from another source such as strontium chromate or dichromate or carbonate.

Below are given examples of baths of this invention. These baths may be modified by adding small concentrations of fluoride, fluosilicate, fluoborate, fluotitanate, fluoaluminate or fluozirconate ions, or boric acid or saturated concentrations of thorium fluoride, thorium fluoborate or fluozirconate, uranium tetrafluoborate, uranium tetrafluozirconate. Also other organic activators such as, for example, trifluoromethyl sulfonic acid, or 2-hydroperfluoroethyl-1 - phosphonic acid ($HCF_2CF_2PO(OH)_2$) can be used together with the Formula A dicarboxylic acids. For example, with 2–6 grams/liter of trifluoromethyl sulfonic acid and/or the 2-hydroperfluoroethyl-1-phosphonic acid, only 0.1 g./l. of the Formula A dicarboxylic acids will show improvement in activation. As high as about 20 grams/liter of the Formula A dicarboxylic acids can be used, though in general the optimum concentrations are from about 0.5 to about 10 grams/liter. The optimum concentration to use depends on the purity and passivity of the nickel plate, and the ratio of the concentration of the chromic acid to the sulfate anion. In most cases the optimum concentration of the Formula A dicarboxylic acid is in the range of 1 to 10 grams/liter. With ratios of chromic acid to sulfate of about 100 to 1 or 90 to 1 very little of these activators is needed but then the chromium coverage is not as great as when the ratio of chromic acid is about 300 to 1 or 200 to 1, or 150 to 1.

Example I

200–400 grams/liter CrO_3
1–1.15 grams/liter SO_4 anion
2–8 grams/liter of tetrachloro succinic acid or perfluoro succinic acid or perfluoro glutaric acid
0–3 grams/liter perfluoro p-ethyl cyclohexyl sulfonic acid
Temp. 40–55° C. (105–130° F.)

Example II

300–400 grams/liter CrO_3
Saturation concentrations of $SrSO_4$ (excess present)
0–50 grams/liter of strontium chromate
1–10 grams/liter of tetrachloro succinic acid, and/or perfluoro succinic acid or perfluoro glutaric acid or perfluoro adipic acid
0–30 grams/liter boric acid
0–5 grams/liter of perfluoro p-ethyl cyclo hexyl sulfonic acid (instead of the strontium salts above, sulfuric acid or other source of sulfate anion can be used to give about 300 to 1 to about 140 to 1 ratio of chromic acid to sulfate).
Temp. 40–60° C. (105–140° F.)

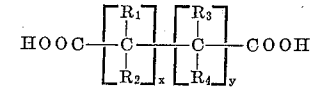
Example III

300–400 grams/liter CrO_3
Saturation concentration of ThF_4 (excess present)
Saturation concentration of $SrSO_4$ (excess present)
Boric acid 1 grams/liter to saturation
1–8 grams/liter of tetrachloro succinic acid or perfluoro succinic or perfluoro glutaric acid or perfluoro adipic acid
0–5 grams/liter of perfluoro p-ethyl cyclohexyl sulfonic acid

In general, the most effective activator is the tetrafluoro succinic acid, and next is perfluoro succinic acid and perfluoro glutaric and slightly less effective is perfluoro adipic. Usually, about 2–4 grams per liter of the tetrachloro succinic will be sufficient for excellent activation with 150 to 1 to 300 to 1 ratios of chromic acid to sulfate and 2 to 8 grams for the perfluoro succinic acid and perfluoro glutaric and 2 to 10 grams/liter for perfluoro adipic acid.

What is claimed is:

1. A bath for the electrodeposition of chromium comprising an aqueous acidic hexavalent chromium plating solution containing a ratio of CrO_3 to sulfate ion greater than about 100 to 1 and less than about 400 to 1 and containing dissolved therein about 0.1 gram/liter to about 20 grams/liter of a dicarboxylic acid characterized by the following formula



where x is selected from 0, 1 and 2 and y is selected from 1 and 2, and when x is 0 and y is 1, R_3 and R_4 are selected from F, Cl, and Br, and when x is 1 and y is 1, R, and R_3 are selected from F and Cl, and R_2 is selected from F, Cl and Br, and R_4 is selected from F, Cl, Br and H, and when $x+y$ is selected from 3 and 4, R_1, R_2, R_3 and R_4 are selected from F and F plus Cl, wherein fluorine atoms at least equal in number the number of chlorine atoms.

2. A bath as claimed in claim 1 and wherein said dicarboxylic acid is tetrachloro succinic acid.

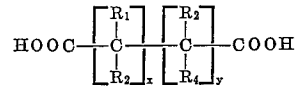
3. A bath as claimed in claim 1 and wherein said dicarboxylic acid is tetrafluoro succinic acid.

4. A bath as claimed in claim 1 and wherein said dicarboxylic acid is hexafluoro glutaric acid.

5. A bath in accordance with claim 1 wherein said hexavalent chromium plating solution is chromic acid in a concentration of about 100 to about 500 grams/liter.

6. A bath in accordance with claim 1 wherein said sulfate ion is derived from saturation concentrations of strontium sulfate in said acidic hexavalent chromimum plating bath.

7. A method of electrodepositing chromium which comprises electrolyzing an aqueous acidic hexavalent chromium plating solution containing a ratio of CrO_3 to sulfate ion greater than about 100 to 1 and less than about 400 to 1 and containing dissolved therein about 0.1 gram/liter to about 20 grams/liter of a dicarboxylic acid characterized the following formula.



where x is selected from 0, 1 and 2 and y is selected from 1 and 2, and when x is 0 and y is 1, R_3 and R_4 are selected from F, Cl, and Br, and when x is 1 and y is 1, R, and R_3 are selected from F and Cl, and R_2 is selected from F, Cl and Br, and R_4 is selected from F, Cl, Br and H, and when $x+y$ is selected from 3 and 4, R_1, R_2, R_3 and R_4 are selected from F and F plus Cl, wherein fluorine atoms at least equal in number the number of chlorine atoms.

8. A method in accordance with claim 7 wherein said dicarboxylic acid is tetrachloro succinic acid.

9. A method in accordance with claim 7 wherein said dicarboxylic acid is tetrafluoro succinic acid.

10. A method in accordance with claim 7 wherein said dicarboxylic acid is hexafluoro glutaric acid.

11. A method in accordance with claim 7 wherein said chromium plating solution is chromic acid in a concentration of about 100 to about 500 grams/liter.

12. A method in accordance with claim 7 wherein said sulfate ion is derived from saturation concentrations of strontium sulfate in said acidic hexavalent chromium plating bath.

References Cited by the Examiner

UNITED STATES PATENTS

2,063,197	12/1936	Schneidewind	204—51
2,517,441	8/1950	Raab	204—51
3,129,149	4/1964	Johnson	204—51 X

JOHN H. MACK, *Primary Examiner.*

G. KAPLAN, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,282,812 November 1, 1966

Henry Brown et al.

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

Column 1, line 42, for "irridescent" read -- iridescent --; column 2, line 16, for "R_1" read -- R_3 --; column 3, line 31, strike out "this"; column 4, line 5, for "1-1.15" read -- 1-1.5 --; line 30, for "1 grams" read -- 10 grams --; column 5, lines 12 to 15, for the upper "R_2" read -- R_3 --.

Signed and sealed this 5th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents