United States Patent Office 3,021,267 Patented Feb. 13, 1962

3,021,267

PLATING BATH AND PROCESS

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No Drawing. Filed Aug. 3, 1960, Ser. No. 47,139
6 Claims. (Cl. 204—51)

This invention relates to chromium plating, and more particularly it relates to chromium plating from a new and improved electrolytic plating bath.

This application is a continuation-in-part of my co-pending application Serial No. 844,877, filed October 7, 1959, now abandoned.

The present commercial chromium plating processes are based on the electrolysis of chromium trioxide, CrO_3 (chromic acid) solutions containing small amounts of a catalyst, e.g., sulfates, fluorides or the like. In such commercial processes, for the production of bright plates of acceptable quality the current density and temperature during plating must be closely controlled. Even when closely controlling the current density, temperature and chromic acid-catalyst ratio, the throwing power of the plating bath is very low as compared to other metal plating processes. Because of poor throwing power, it is necessary to provide anodes conforming to the shape of the object to be plated. Moreover, the current efficiency of the commercial plating baths is usually no greater than 8–12% and under the most optimum conditions only 15 to 20%.

Also, objectionably large volumes of oxygen and hydrogen are given off during plating as a result of which a highly noxious and corrosive spray of chromic acid is always present over the plating bath during the plating operation. Again, large amounts of chromic acid are lost by drag-out and spray due to the necessity of employing rather highly concentrated amounts of chromic acid in commercial baths.

The first chromium deposits were obtained from trivalent chromium solutions more than 100 years ago. Subsequently, many attempts have been made to work out a chrome plating process based on a variety of trivalent and divalent chromium compounds, e.g., sulfates, chlorides, nitrates, fluoborates, acetates, oxalates, tartrates, citrates, cyanides, urea, ammonia, and amines. The early literature on this work is confusing and full of contradictions. Many patents have been issued, only to be discredited by later investigators. In 1933, Kasper at the Bureau of Standards, C. Kasper, J. Research (N.S.B.) 11, 515 (1933), made a critical re-examination on the electrodeposition of chromium from its lower valent oxidation states. He reached the conclusion that none of the reported baths met the moderate requirements of a good plating process and could compete with the chromic acid bath. The divalent chromium baths examined, though more efficient, had a limited brightness range and were easily oxidized by air to the trivalent state. The trivalent baths showed either an extremely low current efficiency or produced plates of poor quality.

It is an object of this invention to provide a new and improved electrolytic chromium plating bath.

It is another object to provide an improved chromium plating bath having a relatively good throwing power and improved current efficiency.

It is yet another object to provide a new and improved chromium plating bath in which the chromium is present in trivalent form.

Another object is to provide an improved electrolytic chromium plating process in which the chromium is present in trivalent form and which will exhibit good current efficiency and throwing power and will produce an excellent bright chromium plate.

Other objects of the invention will become apparent by reference to the following description and claims.

The objects of this invention may be accomplished by preparing an aqueous chromium plating bath comprising a combination of chromic formate and chromic glycolate, sodium formate and sodium glycolate, formic acid and glycolic acid, sodium fluoride, and boric acid. The chromic carboxylates and and the carboxylic acids, and possibly other bath constituents, may be present in the form of a combined complex chemical structure in which chromium has the valence of three, rather than in the presence of simple uncombined compounds. The bath should have a pH of between 2.7 and 4.5.

The electrolytic plating bath of this invention may be operated electrolytically at room temperature or at temperatures up to 90° C. to deposit bright, continuous, highly corrosion-resistant chromium plate. The metallic surface to be plated is first thoroughly cleaned in accordance with cleaning procedures well established in the art. Preferably, the metallic surface to be plated, for example, copper, copper alloys, bronze, brass or nickel surface, is smooth and polished so as to produce a bright chromium plated finish. The metallic object to be plated is suspended as the cathode in the aforesaid electrolytic bath and spaced fairly evenly from an inert anode, such as a carbon, graphite, platinum or platinized titanium anode. The plating may be carried out by passing an electric current of 25 to 300 amperes per square foot between said cathode and anode.

The chromic carboxylates may be the chromic salts of formic and glycolic acids. These carboxylates may be added to the bath as such or they may be formed by dissolving chromic hydroxide or carbonate or even metallic chromium in the carboxylic acids and the pH adjusted with sodium hydroxide or carbonate.

Another convenient way of preparing the chromic carboxylates is based on the reduction of chromic acid (CrO_3) with the formic and glycolic acids in accordance with the equations:

$$2CrO_3+3HCOOH+6H^+ \rightarrow 2Cr^{+++}+3CO_2+6H_2O \quad (1)$$

$$2CrO_3+H_2C(OH)\cdot COOH+6H^+ \rightarrow 2Cr^{+++}+2CO_2+5H_2O \quad (2)$$

If a mixture of formic and glycolic acids is employed in reducing CrO_3, essentially all the reduction is done by glycolic acid according to Equation 2. It may, therefore, be necessary to reduce the CrO_3 separately with these acids and the reduced compositions mixed.

The sodium carboxylates may be added as such or they may be formed in situ in the bath from the carboxylic acids and sodium hydroxide or carbonate.

The carboxylic acids to be added to the bath may be added as such or formed in situ.

The boric acid may be added as borax, boron oxide, boric acid or in the form of the complex compound sodium oxyfluoborate, $4NaF\cdot 5B_2O_3$ (see U.S. Patent No. 2,823,095). All of these materials form boric acid in aqueous solution in the bath.

The sodium fluoride may be added as such, but preferably as the above-mentioned $4NaF\cdot 5B_2O_3$.

The above-named constituents of the electrolytic plating bath of this invention are preferably present in certain proportions. In one liter of plating solution, it is preferred that the several constituents be present in about the following number of gram-moles, depending, of course, upon the particular compounds used, it being understood that the constituents may be present as complex-chemical combinations and reference to amounts of the

following specific compounds is to be regarded from a standpoint of equivalence:

Total chromic carboxylates	0.1 to 1
Molar ratio of total formate to total glycolate	1:8 to 8:1
Total sodium carboxylate and carboxylic acid	0.6 to 7
Boric acid	0.2 to 2
Sodium fluoride	0.2 to 5

Plating experiments in the Hull Cell show that chromium deposits can be obtained under narrowly controlled conditions from solutions containing only chromic formate and sodium formate. These solutions, at a certain current density, start to deposit chromium in the form of a bright plate which, however, turns gray and finally black as the current density increases. The brightness range in such solutions is very limited.

A comparison of fluorine-containing chromic formate baths with chromic glycolate baths and with chromic formate-chromic glycolate mixed baths shows that glycolate baths have a relatively poor current efficiency (approximately 6%) and formate baths have a very limited brightness range and both have a relatively slow plating speed, and they are therefore considered to be without commercial utility. The following three baths are given for comparison.

TABLE I

	Example No. 1—Glycolate-Formate Bath No. B28	Example No. 2—Formate Bath No. B12	Example No. 3—Glycolate Bath No. B2
Total Cr^{+++} [1]	1.0	1.0	1.0
Total Glycolate [1]	1.6	0	3.0
Total Formate [1]	1.4	3.0	0
Total Boron [1]	1.6	1.6	1.6
Total Fluorine [1]	2.2	2.2	2.2
Total Na^+ (exclusive of NaCl) [1]	1.2	1.0	0.9
NaCl [1]	2.4	2.6	2.5
Octyl Alcohol (Weight Percent)	0.15	0.15	0.15
Sodium Salt of saturated long-chain alcohol sulfate	0.15	0.15	0.15
pH	2.75	3.7	3.8

[1] Given in gram-moles per liter.

The best result obtained with the glycolate bath No. 2 was 4 microinches per minute (determined by calculation from area, density and weight gain) at 35° C. and 110 amp./sq. ft. Current efficiency was only about 6%. Although the plate appeared to be bright by itself, when compared with a commercially accepted chromium plate, the plate from B2 had an undesirable gray shade. Only by reducing the plating rate to about 2 microinches per minute could acceptable color be obtained.

The best results obtained with the formate bath No. B12 was a plating rate of 9 microinches per minute of bright chromium with good color at 54° C. and 85 amp./sq. ft. Current efficiency was about 17%. Although better than the glycolate bath, this formate bath was very critical in operation. An increase of only one-third in current density produced unacceptable dark streaks in the plate.

The formate-glycolate bath No. B28 produced a perfect chromium plate at a plating rate of 35 microinches per minute at 60° C. and 220 amp./sq. ft. Current efficiency was about 25%. Many excellent results were obtained with this system at 27°–80° C. and current densities of 30 to 300 amp./sq. ft. At each temperature, however, there is an optimum current density which may be selected by simple trial.

The following examples further illustrate the operating characteristics of the formate-glycolate baths of this invention.

TABLE II

Chromic formate-glycolate baths

Example No.	Bath Composition				pH	Temperature, ° C.	Brightness Range, amp./ft.^{2}
	Cr (III), g. mole/liter	Formate, g. mole/liter	Glycolate, g. mole/liter	$NaF \cdot 1.25B_2O_3$ g. mole/liter			
	M	*M*	*M*	*M*			
4	0.3	0.6	1.5	0.4	4.0	25–35	35–120+
5	0.3	1.1	1.0	0.4	3.5	25–35	90–120+
6	0.3	1.1	1.0	0.4	3.6	25–35	50–120+
7	0.3	1.1	1.0	0.4	3.8	25–35	35–120+
8	0.3	1.1	1.0	0.4	4.1	25–35	30–120+
9	0.3	1.1	1.0	0.4	4.3	25–35	25–120+
	0.3	1.1	1.0	0.4	4.3	30–35	35–120+
	0.3	1.1	1.0	0.4	4.3	40–45	65–120+
	0.3	1.1	1.0	0.4	4.3	55	90–200+
	0.3	1.1	1.0	0.4	4.3	65	100–200+
10	0.3	1.7	0.5	0.33	4.0	25–30	30–120+
11	0.3	2.2	0.3	0.33	4.0	25–30	40–100+

All of the baths of Table II at pH 3.8–4.2 produce bright chromium plates over a broad range of current densities. The current efficiency, however, is markedly affected by the ratio of formate to glycolate in the baths. For example, bath No. 8 produces plates of excellent brightness at 25–45° C. and 30–100 amps. per square foot, but the current efficiency is only 4–6%. Bath No. 11, on the other hand, operates at an efficiency of 18–25% but gives a dull plate around the edges and corners of the work being plated. Bath No. 10, depending upon the operating conditions, has an efficiency of 15–20% and produces a chromium plate of decorative quality at 25–35° C. and 40–100 amps. per square foot. In general, the increase in bath temperature shifts the plating range to higher current densities and lowers the current efficiency. The throwing power in the mixed chromic formate-glycolate baths is generally better than in conventional hexavalent chromic acid baths. In general, it is preferred to have a 1:1 to 1:3 mol ratio of total glycolate to total formate, however, ratios between 1:8 and 8:1 of total glycolate to total formate produce desirable results in accordance with this invention. Total Cr^{+++} means all trivalent chromium, regardless of how combined. Total glycolate means the sum of glycolic acid and glycolate ion, however combined. Total formate, similarly. Total fluoride means all F− added, regardless of whether present as chromium fluoride, BF_3OH^-, HF_2^-, etc. Similarly, total boron refers to that amount synthetically present. Total approximate Na^+ (exclusive of NaCl) is the total of sodium ion added as compounds such as sodium fluoride, plus any added in adjusting pH with sodium carbonate, sodium bicarbonate, or sodium hydroxide, minus any removed to the category of NaCl by adjusting pH with HCl. The "approximate" term is used because the Na^+ concentration should be governed by the pH adjustment. The reason for using a separate category for NaCl is that this is only present to improve the conductivity of the solution.

Its amount may be raised to improve conductivity or reduced at will without any substantial effects on plating characteristics.

From these baths bright chrome plates have been deposited on copper, brass, bronze, and nickel. Deposition directly on steel generally produces dull plates. Copper and its alloys accept my chrome plates very well. A formation of pits is frequently observed in chromium plates, particularly when deposited on nickel, steel, or copper strike on steel. These pits are formed by excessive liberation of hydrogen at some active spots on the substrate surface. The formation of pits can be suppressed by the use of proper anti-pitting agents. For example, the addition of n-octyl alcohol to the bath (approximately 0.5 gram/liter) not only suppresses pit formation but also increases the current efficiency slightly. Higher alcohols ranging from amyl to decyl alcohols give similar results.

The following additional specific example is given to illustrate a preferred embodiment of the invention.

EXAMPLE 12

(*a*) 350 ml. of 98% HCOOH in 200 ml. of water is reacted at 100° C. with 180 g. of CrO_3 dissolved in 500 ml. of water as follows:

The formic acid solution is placed in a 6-liter flask. A few drops of CrO_3 solution are added to the formic acid solution, and the latter is then stirred and heated to boiling. When the reduction of CrO_3 by HCOOH starts (change of color from orange to blue-green), slow addition of CrO_3 solution is continued. Since the reduction of CrO_3 by HCOOH is accompanied by evolution of heat and CO_2 in large quantities, this reaction can be violent when too concentrated reactants are used or when the CrO_3 solution is added too fast. After the addition of CrO_3, the chromic formate solution is kept at the boiling temperature until the reduction of CrO_3 is completed.

(*b*) 300 ml. of 4 molar glycolic acid and 380 ml. of 4 molar sodium glycolate solution are added to the hot chromic formate solution. Glycolic acid will also quickly reduce traces of CrO_3 left in the formate solution.

(*c*) 270 g. of sodium formate (HCOONa) is added to the hot solution.

(*d*) 83 g. NaF and 310 g. H_3BO_3 are mixed and dissolved in 1000 ml. of boiling water. Small amounts of insoluble material (sometimes present in NaF) are filtered off, and the solution is added to the bath.

(*e*) The bath is diluted to 6 liters by water and cooled to room temperature. The pH of the bath is adjusted to between 3.9 and 4.1.

It should be noted that instead of sodium glycolate and formate in steps (*b*) and (*c*) equivalent amounts of glycolic and formic acids may be used, followed by the pH adjustment to 3.9—4.1 with sodium hydroxide or carbonates.

The electrolytic plating baths of this invention have been used to plate copper, brass, bronze, and nickel using carbon, graphite, platinum and platinized titanium-insoluble anodes to obtain bright chromium plates. The plating may be carried out at current densities of 25 to 300 amps./ft.^{2} at 25–35° C. with a cathodic current efficiency of 15–20% based on trivalent chromium. (Based on hexavalent chromium, these current efficiencies are 30 to 40%.) Any pitting of chromium plate may be eliminated by the addition of a small amount of a higher alcohol having 5 to 12 carbon atoms, for example, n-octyl alcohol.

With the aforementioned insoluble anodes, anodic oxidation of Cr (III) to the hexavalent state occurs to a slight extent. The accumulation of hexavalent chromium in the baths, however, is undesirable because it

decreases the current efficiency markedly, as shown in the following example:

Ratio of Cr (VI)/Cr (III) in the Baths	Efficiency, percent
0–0.01	18
0.04	9
0.1	Below 1

The accumulation of hexavalent chromium in the bath can be eliminated by occasional heating of the bath to speed up the reduction of Cr (VI) by glycolic and formic acids or by employing a two-compartment cell separated by an ion exchange membrane permeable only to cations.

The chromium plating solutions of this invention show a medium electrolytic conductivity, i.e., about 0.05 mho/cm. at 25° C. For comparison, the standard nickel sulfate-chloride bath has a specific conductivity of 0.084 mho/cm. at 55° C. and pH 3.8. The electrolytic conductivity of plating baths can be increased either by raising the temperature or by adding an inert electrolyte to the bath. For example, after the addition of sodium chloride in amounts to make the bath 0.5 and 1.0 molar in sodium chloride, the conductivity of the baths rose to 0.075 and 0.092 mho/cm. at 25° C., respectively. Addition of sodium sulfate or sulfamate gave similar results. Furthermore, it was found that these anions did not affect the plating characteristics and the current efficiency even when added in stoichiometric amounts for the formation of the corresponding chromic compounds.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

I claim:

1. An aqueous electrolytic plating bath for the plating of bright chromium plate, said bath comprising a mixture of chromic formate, chromic glycolate, formic and glycolic acids, sodium formate and sodium glycolate, sodium fluoride, and boric acid, said bath having a pH of between 2.7 and 4.5 and containing, per liter, a total of between 0.1 and 1 gram-mole of said chromic carboxylates, a total of between 0.6 and 7 gram-moles of said sodium carboxylates and carboxylic acids, between 0.2 and 2 gram-moles of boric acid and between 0.2 and 5 gram-moles of sodium fluoride.

2. An aqueous electrolytic plating bath as defined in claim 1 in which the mol ratio of total formate to total glycolate is between 8:1 and 1:8.

3. An aqueous electrolytic plating bath as defined in claim 1 in which the mol ratio of total formate to total glycolate is approximately 1:1 to 1:3.

4. The process for the electroplating of bright chromium which comprises passing a direct electric current with a current density of 25 to 300 amp./sq. ft. between an inert anode and a metallic cathode in an electrolytic plating bath comprising a mixture of chromic formate, chromic glycolate, formic and glycolic acids, sodium formate and sodium glycolate, sodium fluoride, and boric acid, said bath having a pH of between 2.7 and 4.5 and containing, per liter, a total of between 0.1 and 1 gram-mole of said chromic carboxylates, a total of between 0.6 and 7 gram-moles of said sodium carboxylates and carboxylic acids, between 0.2 and 2 gram-moles of boric acid and between 0.2 and 5 gram-moles of sodium fluoride.

5. The process for the electroplating of bright chromium as defined in claim 4 in which the mol ratio of total formate to total glycolate is between 8:1 and 1:8.

6. The process for the electroplating of bright chromium as defined in claim 4 in which the mol ratio of total formate to total glycolate is approximately 1:1 to 1:3.

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