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PLATING BATH AND PROCESS

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

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.

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

It is another object to provide a new and improved chromium plating bath that will have greatly improved throwing power and improved current efficiency.

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

It is another object to provide a new and improved chromium plating bath that will have a greatly broadened plating range within which bright chromium plates will be obtained.

Another object is to provide a new and improved plating process in which chromium is plated from a plating bath containing chromium in trivalent form and which will exhibit good current efficiency and throwing power and will produce excellent bright chromium plate.

Other objects of the invention will appear hereinafter.

The above objects may be accomplished, in general, by preparing an electrolytic aqueous chromium plating bath comprising chromic carboxylate, a carboxylic acid and boric acid. The chromic carboxylate and the carboxylic acid, and possibly other bath constitutents, appear to be present, to a considerable extent, in the form of a combined complex chemical structure in which chromium has the valence of three. The bath should have a pH value between 1.5 and 3.0.

In the copending patent application of Talivaldis Berzins, Serial No. 844,877, filed of even date herewith, now abandoned, a chromium plating bath and process is described and claimed in which the aqueous electrolytic chromium plating bath comprises a chromic carboxylate, sodium carboxylate, a carboxylic acid, sodium fluoride and boric acid, and in which the pH is between 3.5 and 4.5.

Although the bath of this invention differs from the

Berzins bath only in the preferred exclusion of a fluoride, the presence of little or no alkali carboxylate, and a different pH, it appears that the complex compounds present in the two baths differ greatly from each other. This is evidenced by the fact that the pH value of 3.5 to 4.5 of the Berzins bath will produce exceedingly poor or no plating whatever if employed in this bath and vice versa if the pH value of 1.5 to 3.0 of this bath is employed in the Berzins bath no useful plating can be accomplished. Moreover, the bath of this invention excels outstandingly the Berzins bath in the working range which can be attained with good current efficiency.

The electrolytic plating bath of this invention may be operated electrolytically at room temperature or temperatures as high as 65° 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 200 amperes per square foot between said cathode and anode.

The plating baths of this invention are greatly superior to commercial hexavalent chromium plating baths in current efficiency, throwing power and plating range. These terms are, for convenience, defined as follows:

"Current efficiency" is generally defined as the ratio of weight of metal actually deposited by a given current for a given time to that which would have been deposited if electro-reduction of the desired metal were 100% efficient. The latter is calculated from Faraday's law, which says that 96,500 coulombs (ampere-seconds) is required to electrodeposit one gram equivalent of metal, if no side-reactions occur such as liberation of hydrogen. Current efficiency is commonly expressed as percent. It is important to note that current efficiencies as thus calculated are not directly comparable between VI, III, and II-valent chromium. Thus, the best that could possibly be deposited by 96,500 coulombs from hexavalent, trivalent, and divalent chromium salts are, respectively, 52÷6, 52÷3, and 52÷2 grams. Thus a current efficiency of 15% with a trivalent bath is just as good as 30% with a hexavalent bath, or only as good as 10% with a divalent bath. Current efficiency is important because it governs in part the rate of plating, and so is of great economic importance. However, the cost of current is only one factor in the economics of plating. Probably of more practical importance is the maximum speed of plating, using as much current as will be tolerated without appearance of defects discussed below under "plating range."

"Throwing power" is a term used in the plating industry to signify the degree to which plating occurs in recesses or on surfaces which are remote from the anode as compared with plating on flat surfaces or those near to the anode. Everyone in the plating industry knows what "good throwing power" is, and that commercial chromium plating baths have very poor "throwing power." However, there does not appear to be a generally accepted measure of "throwing power" as such. To a principal degree the differences in plating on the variously disposed surfaces of an article in a plating bath are governed by the response of the plating system to the local current densities. Therefore, we can secure good information about "throwing power" by measuring "plating range."

It is frequently true of electroplating baths that below certain current densities (amperes per unit area) they either do not deposit metal at all, or if they deposit metal, it is defective in brightness, color, or other respect. Above an upper limiting current density characteristic of each specific bath the plating is "burned" or discolored, matt, spongy, or otherwise defective. Between these limits, which I will call "threshold current density" and "ceiling current density," good plating occurs. It is evident that if this range is very narrow, the system will have "poor throwing power." This is a present handicap in commercial chromium plating. It is also evident that if this range is very broad and the "ceiling current density" occurs at very heavy currents, then plating can be very rapid, even if current efficiency is only moderately good.

Chromic carboxylate of the bath may be the chromic salt of a carboxylic acid, for example, the chromic salt of glycolic, lactic, formic or oxalic acids or mixtures thereof. The preferred chromic carboxylates are chromic salts of alpha-hydroxy carboxylic acids for example, glycolic and lactic acids, the cromic glycolate having given the best results. These carboxylates may be added to the plating bath as such or they may be formed in the bath by dissolving chromic hydroxide or carbonate or even metallic chromium in the carboxylic acid and the pH adjusted with sodium hydroxide or carbonate.

A convenient way of preparing the chromic carboxylates is based on the reduction of chromic acid (CrO_3) with the carboxylic acid, for example, glycolic acid, in accordance with the equation:

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

with the glycolic acid being present in sufficient amount to form a complex chromic compound that appears to correspond with the following reaction:

$$2CrO_3+3H_2C(OH)\cdot COOH\rightarrow 2Cr(CO_2\cdot CH_2OH)(OH)_2+2CO_2+H_2O$$

Preferably the glycolic to chromic ion ratio is maintained between 1.1 to 1 and 2.1 to 1. However, as the ratio of glycolic acid is increased in this range, the "threshold current density" increases undesirably. One might expect that large amounts of glycolic acid could be added if amounts of sodium glycolate were added to keep the pH the same. Surprisingly, this is not the case. Large amounts of unionized glycolic acid or other acids (even at unchanged pH) undesirably raise the "threshold current density." I believe this is caused by a competing useless reaction at the cathode which liberates hydrogen from the unionized acid.

If it is desired to obtain plating at a minimum current density, the excess glycolic acid (over a ratio of 1 glycolic to 1 chromium) should be small. If maximum current efficiency is desired, this ratio may be somewhat increased in the range specified.

Some satisfactory plates have been obtained when the carboxylic acid is formic or oxalic, or mixtures of these with glycolic acid. The properties of these plating systems are inferior to those containing only glycolic acid, either in current efficiency or plating range or brilliance of plate.

The concentration of chromium in the plating bath is suitably 0.5, 1, or 1.5 moles per liter. Results do not depend very critically on concentration. The concentration of carboxylic acid is specified by this and the ratio cited above.

Whereas in the aforesaid Berzins process exceptionally desirable results were obtained from a mixture of formic and glycolic acids and the resulting mixture of chromic formate and glycolate, the present process operates in a superior manner by the use of glycolate alone but with the use of a salt of a strong acid to furnish the necessary bath conductivity, as set forth in greater detail below.

Whereas in the aforesaid Berzins process the bath contains considerable amounts of alkali carboxylates, the bath of the present process contains smaller amounts. For example, at 1 molar free glycolic acid and pH 2.4 in the present bath, free glycolate ion cannot exceed 0.04 mole per liter, as calculated from the dissociation constant of glycolic acid at 25° C.:

$$\frac{\text{Hydrogen ion}\times\text{glycolate ion}}{\text{Glycolic acid}}=1.5\times10^{-4}$$

It is possible to use alkali glycolates in large amounts in making up the bath, but it will be evident that by the time the pH has been adjusted by adding a strong acid such as hydrochloric acid, the alkali glycolate will have been largely converted to free glycolic acid and alkali chloride as governed by the above dissociation constant.

The boric acid may be added as borax, boron oxide, or boric acid. Without the presence of boric acid, bright chromium plating can be obtained only within an impractically narrow range of current densities. Boric acid expands this range tremendously. It is preferred to use it at as high a concentration as possible within the limit of solubility; that is, about one mole per liter.

While the principal difference between this process and that of said Berzins application resides in the difference in pH ranges, and correspondingly in the ratios of free carboxylic acids to alkali carboxylates in the solution, it is also found that fluorides, which are essential in the Berzins process, are not essential to my process. In fact, addition of fluorides to my solution is somewhat detrimental by reason of an increase in the threshold current density required to start plating. It is known that hydrogen fluoride is a weak acid with first dissociation constant of about 7×10^{-4}. The detrimental effect of added fluorides in my plating baths may be due to the fact that the pH range 1.4 to 3.0 fluorides must be reacted largely to form un-ionized hydrogen fluoride or HF_2^- ions.

The plating bath of this invention needs the addition of an alkali metal salt of a strong acid. The water solution of the chromium complex formed in this bath has a very low electric conductivity. The alkali metal salt of a strong acid is necessary to furnish the conductivity required for practical electroplating. The cation of the aforesaid salt can be sodium or potassium, the latter being preferred for higher conductivity. The strong acid anions should be those of an acid having a dissociation constant of at least $K=10^{-2}$, for example, perchlorate, chloride, sulfamate, or sulfate-bisulfate mixtures. The strong acid anions should be anions that are not reduced at the cathode during the electroplating operation. It appears that the stronger the acid corresponding to the electrolyte is, the better the results, especially in regard to breadth of plating range and brilliance of plate with freedom from haze. The concentrations of alkali salts of in the pH range 1.4 to 3.0 fluorides must be reacted largely to form unionized hydrogen fluoride or HF_2^- ions.

In some cases, some of the above-mentioned anions cause problems at the anode. For example, chloride ions liberate noxious chlorine at the anode, or in the case of perchlorate ions, the chromium complex may be oxidized electrically at the anode to hexavalent chromium which is detrimental to plating performance. These difficulties may be partly avoided by placing the anode in a separate compartment with a porous diaphragm to limit mixing of the solution from the anode and cathode regions. These difficulties may be completely avoided by isolating the anode within a cation-permeable membrane. Several companies make a cloth coated with a cation exchange resin for this purpose; such membranes are rugged, low in electrical resistance, and permit cations to penetrate freely while anions are barred. Under such conditions any convenient electrolyte, for example, dilute sulfuric acid may be used in the anode bag or compartment.

The above-named constituents of the electrolytic plating bath of this invention are preferably present in certain

proportions. In 1000 grams 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 ion	0.1	to 1
Total carboxylic acid, free and combined	0.07	to 3
Boric acid	0.2	to 2
Alkali metal salt of strong acid	0.2	to 3

The chromium plating bath of this invention is maintained at a pH between 1.5–3.0 and preferably between 2.0–2.7. If the pH is reduced, the threshold current density increases. This may be undesirable if carried too far. However, plating efficiency and plating range generally increase somewhat. If pH is raised, the reverse effects occur. There is no single pH at which all plating may be carried out at best results; however, in general, when the pH reaches 3.5 nearly all plating ceases.

With regard to pH adjustment, this is done by adding an alkali metal hydroxide, carbonate or bicarbonate to raise pH. The strong acid corresponding to the said alkali metal salt of a strong acid may be used to go the other way. It is to be noted that the basic chromium carboxylate, such as $Cr(CO_2 \cdot CH_2OH)(OH)_2$, gives an acidic reaction in water, usually falling within the above pH range without further adjustment.

In measuring or adjusting pH it should be noted that pH tends to drift after each addition of acid or base. It is believed that this is caused by slow equilibration of the chromium complexes in the solution. Therefore, it is expedient, after an adjustment, to heat the solution to boiling, and then cool it before measuring the pH.

It has been found desirable to exclude from the plating bath of this invention acids having a dissociation constant of between about 10^{-2} and 10^{-6} and their salts, other than the carboxylic acids specified in amounts to be present at a ratio to chromic ion of 0.7 to 1 to 3 to 1, or preferably 1.1 to 1 to 2.1 to 1. Such acids and salts appear to raise the threshold current density at which the bath may be used to obtain bright plates.

In preparing the plating bath of this invention, one mole of chromic acid (CrO_3) may, for example, be reacted with 1.6 moles of glycolic acid. To reduce the chromic acid, 0.5 mole of glycolic acid is needed, 1.0 mole is present to form the desired complex and 0.1 mole for excess. If materially less than 1.5 moles of glycolic acid is used, the chromic acid may not all be reduced, and the residue may be detrimental for further work. The chromic acid, dissolved in water, should be cautiously added to the glycolic acid dissolved in water at 90–100° C. When all added, the solution should be boiled for one hour to complete the reaction. It is very undesirable to reverse the order of addition, because then the reaction mixture sets to a gel before all the glycolic acid is added.

The product of the reaction is a deep green solution which evaporates to a non-crystalline green glassy material. This material appears to be a basic chromium glycolate complex containing one gram mole of glycolic acid per gram atom of chromium, together with about 0.1 mole of free glycolic acid.

With the chromium glycolate complex prepared as above, commercial chemicals are used to make up the rest of the bath. After mixing these, the solution is heated to boiling and then cooled to equilibrate the various chromium complexes that may be present in the bath.

The following examples are given to illustrate certain preferred embodiments of the invention:

Examples I and II

[Gram moles per liter of solution]

	I	II
Potassium sulfamate, KSO_3NH_2	1.6	2.8
Sulfamic acid, HSO_3NH_2	0.2	
Boric acid, H_3BO_3	1.0	1.0
Trivalent chromium,[1] Cr^{+++}	1.0	0.5
Glycolic acid,[1] $CH_2OH \cdot COOH$	1.2	0.6
Octyl alcohol	0.01	0.01
	pH 2.30	pH 2.30

[1] From a solution of $Cr(CH_2CO_2)(OH)_2$ containing 10% excess glycolic acid.

Brass plated with I acquired a bright chromium plate within the current density range from 25 to over 200 amp./sq. ft. In the upper end of this range the plate appeared a little hazy. Plating efficiency at 100 amp./sq. ft., as calculated from weight gain, was about 10% (as good as 20% with a hexavalent chromium bath).

Brass plated with II developed a bright chromium plate within the current density range from 25 to over 200 amp./sq. ft., with only a trace of haze at the upper end of the range. Plating efficiency at 100 amp./sq. ft. was about 7%.

The octyl alcohol is added to improve smoothness and prevent pitting.

Example III

[Gram moles per liter]

	III
Potassium chloride, KCl	2.0
Trivalent chromium, Cr^{+++}	1.0
Glycolic acid, $CH_2OH \cdot COOH$	1.2
Boric acid, H_3BO_3	1.0
Octyl alcohol	0.01
pH 2.67	

Nickel plated with this solution developed an extremely bright chromium plate from 18 to over 200 amp./sq. ft. There was no trace of haze. Plating solutions of this type commonly yielded 10 to 17% current efficiency at 100–200 amp./sq. ft.

Example IV

	IV
Sodium perchlorate, $NaClO_4$	2.0
Trivalent chromium, Cr^{+++}	1.0
Glycolic acid, $CH_2OH \cdot COOH$	1.2
Boric acid, H_3BO_3	1.0
Octyl alcohol	0.01
pH 1.90	

Brass plated with this solution developed an extremely bright chromium plate from 18 to over 200 amp./sq. ft. There was no trace of haze. Current efficiency was about 4%.

Example V

[Gram moles per liter of solution]

Potassium sulfamate, KSO_3NH_2	1.2
Boric acid, H_3BO_3	0.8
Trivalent chromium,[1] Cr^{+++}	1.0
Lactic acid,[1] $CH_3 \cdot CHOH \cdot COOH$	2.1
pH 2.38	

[1] From a solution containing 1 mole of total chromium and 2.1 moles of total lactic acid per liter.

Brass plated with the above electrolyte acquired a very bright chromium plate with a current density of from 36 to over 120 amperes per square foot.

Example VI

[Gram moles per liter of solution]

Sodium sulfate, Na_2SO_4	1.0
Boric acid, H_3BO_3	0.7
Trivalent chromium,[1] Cr^{+++}	1.0
Sodium binoxalate,[1] $NaHC_2O_4$	1.0
Oxalic acid,[1] $H_2C_2O_4$	1.0
pH 1.82	

[1] Made by adding sodium hydroxide to a solution containing chromium (III) oxalate and free oxalic acid.

Brass plated with this electrolyte acquired a smooth chromium plate over the current density range of 50 to over 120 amperes per square foot. The color was not as brilliant as in the other examples given. Current efficiency was about 6%.

The electrolytic plating baths of this invention may be 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 10 to 200 amps./sq. ft. at 20° C. to 65° C. with a cathodic current efficiency of 5 to 25% based on trivalent chromium. (Based on hexavalent chromium; these current efficiencies are 10 to 50%.) 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.

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 per 1000 g. of bath an amount of chromium glycolate to provide the bath with 0.1 to 1 gram-mole of chromic ion, 0.07 to 3 total gram-moles of glycolic acid, 0.2 to 3 gram-moles of an alkali metal salt of an acid having a dissociation constant of at least $K=10^{-2}$, and 0.2 to 2 gram-moles of boric acid, said bath being substantially free from fluorine, having a pH of between 1.5 and 3.0, and in which the molar ratio of carboxylic acid to chromium is between 0.7:1 and 3.0:1.

2. An aqueous electrolytic plating bath for the plating of bright chromium plate, said bath comprising per 1000 g. of bath, an amount of chromium glycolate to provide the bath with 0.1 to 1 gram-mole of chromic ion, 0.07 to 3 total gram-moles of glycolic acid, 0.2 to 3 gram-moles of an alkali metal salt of an acid having a dissociation constant of at least $K=10^{-2}$, and 0.2 to 2 gram-moles of boric acid, said bath being substantially free from fluorine, having a pH of between 2.0 and 2.7, and in which the molar ratio of carboxylic acid to chromium is between 1.1:1 and 2.1:1.

3. The process for the electroplating of bright chromium which comprises passing a direct electric current with a current density of 10 to 200 amps./sq. ft. between an inert anode and a metallic cathode in an electrolytic plating bath comprising per 1000 g. of bath an amount of chromium glycolate to provide the bath with 0.1 to 1 gram-mole of chromic ion, 0.07 to 3 total gram-moles of glycolic acid, 0.2 to 3 gram-moles of an alkali metal salt of an acid having a dissociation constant of at least $K=10^{-2}$, and 0.2 to 2 gram-moles of boric acid, said bath being substantially free from fluorine, having a pH of between 1.5 and 3.0, and in which the molar ratio of carboxylic acid to chromium is between 0.7:1 and 3.0:1.

4. The process for the electroplating of bright chromium which comprises passing a direct electric current with a current density of 10 to 200 amps./sq. ft. between an inert anode and a metallic cathode in an electrolytic plating bath comprising per 1000 g. of bath an amount of chromium glycolate to provide the bath with 0.1 to 1 gram-mole of chromic ion, 0.07 to 3 total gram-moles of glycolic acid, 0.2 to 3 gram-moles of an alkali metal salt of an acid having a dissociation constant of at least $K=10^{-2}$, and 0.2 to 2 gram-moles of boric acid, said bath being substantially free from fluorine, having a pH of between 2.0 and 2.7, and in which the molar ratio of carboxylic acid to chromium is between 1.1:1 and 2.1:1.

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