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Bride

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[54] **PREPARING PLATING BATH CONTAINING CHROMIC COMPOUND**

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[58] **Field of Search** 204/51

[56] **References Cited**

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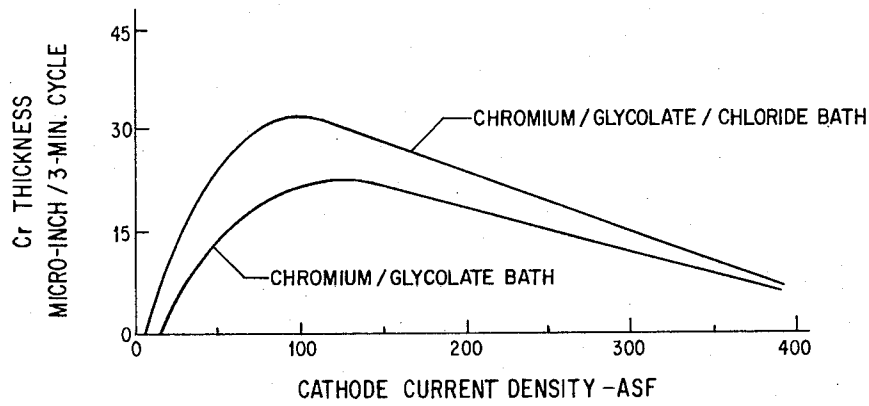
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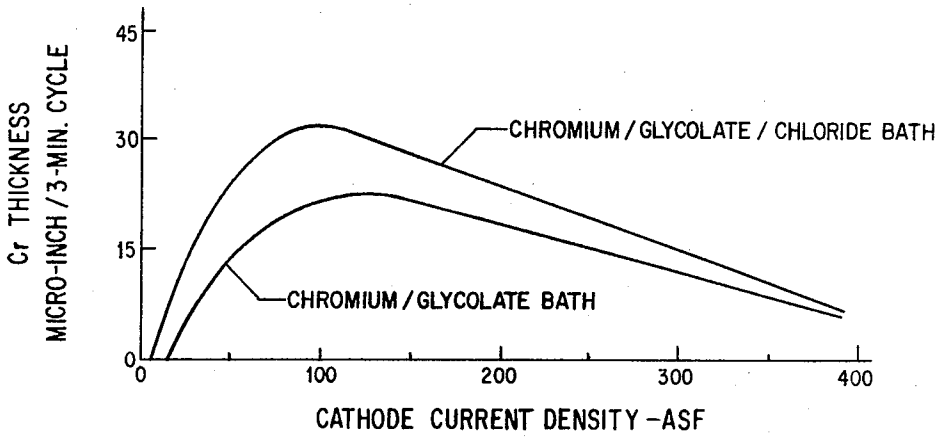
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[57] **ABSTRACT**

A bright decorative chromium plate of good appearance and durability is electrodeposited from a bath prepared from a solution containing trivalent chromic-compound. More particularly the bath is made from a preformed complex, or such complex is made in situ, and is a water-soluble trivalent chromic compound containing carboxylic acid constituents and halogen constituents. The prepared bath provides for excellent plating speed in the low current density region thus offering enhanced chromium thickness in recessed and difficult to plate areas.

17 Claims, 1 Drawing Figure





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PREPARING PLATING BATH CONTAINING CHROMIC COMPOUND

BACKGROUND OF THE INVENTION

Decorative chromium plating from baths which contain chromium in the trivalent state have been extensively investigated. However it has been found difficult in commercial practice to prepare such a bath that will compete successfully with the decorative plating baths, containing chromium in the hexavalent state, which have received wide commercial acceptance. For example U. S. Pat. No. 3,006,823 describes a recently developed aqueous electrolytic plating bath containing a chromium complex of chromic ion and particular carboxylic acid. Although such bath is of interest, the plating performance, for example in the low current density area, can be undesirable.

SUMMARY OF THE INVENTION

A decorative chromium plating bath has now been developed which in addition to providing a highly desirable bright range and a decorative plate with a desirable bright finish, shows excellent plating speed in the low current density region.

Broadly the method of the invention is directed to preparing an aqueous electrolytic plating bath for the plating of bright chromium plate upon articles contacted therewith, which method comprises: establishing an aqueous medium containing a complex, water-soluble chromic compound containing carboxylic acid constituents and halogen constituents selected from the group consisting of chlorine, fluorine, bromine, iodine or mixtures thereof, with such compound supplying not substantially above about 150 grams of chromium per liter of the medium; adjusting the pH of such medium within a range of between about 1.8 and about 4.9; while maintaining the temperature of said medium not substantially in excess of about 50°C.

The invention is further directed to methods of preparing aqueous electrolytic plating baths for the plating of bright chromium plate by first preparing a complex, water-soluble chromic compound.

BRIEF DESCRIPTION OF THE DRAWING

The drawing presents in graphic form and for comparative purposes, thickness of chromium deposit from a bath prepared according to the present invention and also from a comparative bath containing a comparative trivalent chromium complex.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

One of the consistent and most noticeable effects achieved by the plating baths prepared in the present invention is exemplified in the drawing which is a plot of chromium plating thickness versus the cathode current density. The plating thickness shown is in microinches for a three minute plating cycle using 10 amperes of current in a modified Hull cell, such cell being explained more fully hereinafter. The cathode current density is given in amperes per square foot (ASF) of cathode.

In the drawing, two plots are shown, the upper graph line showing the thicker deposit of chromium, most especially in the lower current density region, achieved

for a bath prepared according to the present invention and containing a complex of chromium with carboxylic acid constituent from glycolic acid and with chlorine supplying the halogen. The lower line on the graph depicts the plate thickness achieved in a comparative bath, such as described in U. S. Pat. No. 3,006,823, and containing a comparative chromic carboxylate complex of chromium with glycolic acid. More detailed description of the plating conditions employed in the tests represented by the plots in the drawing, are given hereinafter in connection with the examples.

The chromic compound for preparing the bath according to the present invention contains halogen constituents that can be chloride, fluoride, bromide, iodide or mixtures thereof. However, in typical plating operation, bromine and iodine are often not used, for economy and to avoid evolution of visible noxious fumes at the anode. Therefore chlorine, fluorine and their mixtures are preferred in preparing the complex. When the halogen is not supplied by a chromic compound, as will be more particularly discussed hereinbelow, it is preferably, for economy, supplied simply as the acid, e.g., hydrogen chloride or hydrogen fluoride. However, other substances may be used and these include gaseous chlorine, gaseous fluorine, and sodium fluosilicate.

The carboxylic acid constituent for the complex is most typically supplied by a carboxylic acid having less than about 10 carbon atoms, and being a saturated acid free from carbon-to-carbon unsaturation. The acid is a dicarboxylic acid, or a monocarboxylic acid, or such dicarboxylic and monocarboxylic acids containing at least one hydroxyl group, or mixtures of these acids. Representative such acids which can or have been used most usually have less than about six carbon atoms and include glycolic acid, lactic acid, oxalic acid, and their mixtures. Preferably for enhanced plating performance plus economy the carboxylic acid constituent is supplied at least in major amount by glycolic acid. A compound of any of the carboxylic acids, such as a salt or an ester thereof, which will act in any of the reactions whereby the complex is formed, in the same manner as the free acid, can be used.

The plating baths where the complex is formed in situ can be prepared by any of several methods. One method is the straightforward combination of chromium metal with carboxylic acid plus halogen-providing compound, for example hydrochloric acid. When such combination includes particulate chromium metal to reduce reaction time, the reaction can be highly exothermic, and therefore caution needs be taken in carrying out same. Typically for enhanced reaction efficiency, as the reaction proceeds and the evolved heat starts to diminish, external heating is applied, and such external heating may involve refluxing of the reaction mixture if such complex is being prepared in concentrated form for later dilution with further aqueous medium and concomitant bath formation.

The complex may also be prepared from the carboxylic and halogen-providing compound in admixture with chromic acid, typically charged to the reaction medium as a solution of chromic acid in water. In an aqueous reaction medium, the chromic acid can be supplied by any of the suitable substances for forming chromic acid in water, e.g., chromium trioxide. The reaction resulting from this method is also exothermic

and caution in the use of such method is thus advisable. As a further aspect of this method, chromic acid, for example, may be first reacted with halogen-providing compound such as hydrochloric acid to prepare a preformed reaction medium. To this medium carboxylic acid is added, preferably with heating to hasten completion of the reaction for final complex formation. In this reaction fugitive liquid can form a portion of the reaction medium, with water that may be supplied from the halogen-providing substance, e.g., a 20 to 37 weight percent solution of HCl in water providing the balance of the liquid medium. For the fugitive liquid, a secondary alcohol such as isopropanol is preferred, as taught in U. S. Pat. No. 2,524,803, and preferably one of no more than four carbon atoms, as such alcohol does not coordinate with the chromium and can be readily removed from the product by processes familiar in such art, e.g., evaporation with accompanying crystallization followed by water washing. The subsequent reaction medium for carboxylic acid addition is then an aqueous medium.

The complex may further be prepared by reaction of chromic halide, and carboxylic acid, with such halide corresponding to the halide that is to be present in the complex. When chromic halide is reacted with the carboxylic acid, this reaction further involves the addition of strong base, e.g., an alkali metal hydroxide, yielding hydroxyl ions in the aqueous reaction medium. For example, $CrF_3 \cdot 9H_2O$ may be used in this method and will readily yield a chromium/carboxylic acid/fluoride complex involving exothermic reaction conditions.

The complex virtually always contains a molar ratio of chromium atoms to carboxyl constituent within the range of 1:0.7 to 1.3, and further contains a molar ratio of chromium atoms to halogen atoms within the range of 1:0.1 to 1:3.5. Especially preferred ratios, based upon desirable performance and economy, can depend upon the acid as well as the halogen constituents of the complex. Thus, for example, for a complex containing a substantial amount of the carboxyl constituents supplied by glycolic acid, which complex is thus the preferred complex, and wherein such complex further contains chloride as the major amount, to all, of the halogen, the molar ratio of chromium atoms to halogen is preferably within the range of about 1:0.4 to 1:1. However when the halogen in such a complex is preponderantly to all fluoride, the molar ratio of chromium atoms to halogen atoms is preferably within the range of about 1:2.6 to 1:3.2. Further, the ratio of chromium to halogen can depend upon the method of complex preparation. For example in the above mentioned preparation method employing the $CrF_3 \cdot 9H_20$, the resulting complex will contain a molar ratio of chromium to moles of fluorine of 1:3. From this it can be appreciated that complex formation relying completely upon a chromic halide or a basic chromic halide, e.g., $Cr(OH)Cl_2$, will always yield a complex wherein the molar ratio of moles of chromium to moles of halogen will be within the broad range of 1:0.7 to 1:3.

The complex is furnished to the plating medium in an amount to provide from about 25 to about 150 grams of chromium per liter, that is, the molar concentration of chromium in the plating medium is within the range from about 0.5 to about 3. The more highly concentrated media having augmented viscosity are not well suited for deposition of chromium onto a metal substrate which is immersed therein. Thus such media having a molar concentration of chromium above about 1.5 may be employed in portable plating devices used in spot plating, e.g., for brush plating, but for bath operation wherein the article is immersed in a bath, such baths most always contain an amount of complex providing from about 25 to about 75 grams of chromium per liter. Within this concentration range the bath will be supplied with sufficient complex to avoid frequent bath replenishment during working. In this bath the complex is virtually always used in a liquid medium supplied simply by water although other liquids may be present, e.g., excess carboxylic acid other than such acid resent in the complex, but these other liquids will constitute a minor amount of the liquid medium of on the order of about five volume percent or less.

Before deposition of chromium, the medium is adjusted to a pH within the range from about 1.8 to 4.9. Such adjustment of pH can be readily carried out with a base, particularly alkali metal carbonates or hydroxides, with sodium or potassium hydroxide or their mixtures being preferred. Before addition to the medium, such material for pH adjustment can be initially dissolved in water and the water solution then added to the medium.

The bath can also be furnished with a salt of a strong acid preferably, for economy, an alkali metal salt. Such salts enhance the conductivity achieved in the electroplating operation. Most preferably, for economy, the cation of the salt is sodium, potassium or their mixtures, and the strong acid anions should be those of an acid having a dissociation constant of at least $K=10^{-2}$, for example, chloride. The plating bath usually contains between about 50-200 grams per liter of such salts. The bath can also be provided with boric acid, or an equivalent to boric acid in an aqueous solution, such as borax, boron oxide, or sodium oxyfluoborate. Such compounds operate in the bath to augment the rate of deposition of the chromium and are typically used in an amount between about 10–70 grams per liter of bath.

The temperature of the medium during plating may range from about 20°C. up to advantageously not substantially above about 50°C. for enhanced plating performance. The most desirable pH range and temperature range can depend upon the make-up of the complex present in the plating medium, with, for example, complex containing a substantial amount of fluorine as the halogen being in a bath that is preferably maintained at a slightly more elevated temperature than for a bath where chlorine supplies the major amount of the halogen.

For the baths prepared as described herein, the object to be plated is made the cathode, for example immersed in the plating bath, or the cathode in a brush plating operation where the plating medium is contained in the brush, and an inert anode is used such as a carbon, graphite, platinum or platinized titanium anode. In working of the bath a small discharge of halogen, e.g., gaseous chlorine, and trivalent chromium fume may be given off at the anode. However, halide replenishment as well as replenishment of all chromium, including that plated from the bath or lost by drag-

out, is adequately taken care of by addition of further complex. Likewise such addition of complex can adequately replenish any acid which may be used up in the plating operation during working of the bath.

The substrates which may be employed during operation of the bath includes metals such as steel, brass, copper, copper alloys, bronze, zinc diecastings, as for example to prevent rusting or tarnishing, or nickel surfaces. Additionally plating can be performed on plastic surfaces which are activated or prepared for an electroplating operation. The plating bath can be prepared and the subsequent plating carried out in any vessel useful for chromium electroplating such as tanks lined with corrosion resistant material including glass, ceramic material, polyvinyl chloride, and the like.

The following examples show ways in which the invention has been practiced but should not be construed as limiting the invention. Unless otherwise specified, plating tests in the examples are conducted in a modified Hull cell. The standard Hull cell is a trapezoidal box of non-conductive material at the opposite ends of which are positioned anode and cathode plates, as has been more particularly described in U. S. Pat. No. 2,129,344. For either the standard or the modified Hull cell, it is possible to easily determine the effective plating range of a plating composition under varying conditions. The current density at any point on a cathode is determined according to the formula $A=C(2\ 7.7\text{-}48.7\ \log\ L)$ wherein A is the current density in amps per square foot (ASF) at the selected point, C is the total current in amps applied to the cell and L is the distance in inches of the selected point from the high current density end of the plate.

In the modified version of the Hull cell used herein, ½-inch holes are introduced in the parallel sides of the cell adjacent the anode and cathode whereby, upon immersion of the cell in another containing plating solution, into which vessel the cell will fit very closely, improved electrolyte circulation and consequent improved temperature control is afforded, as more particularly described in an article appearing in "Plating" Volume 46, Number 3 (1959) Page 257.

EXAMPLE 1

Into a container there is placed 0.8 mole of chromium metal, 1.8 mole of glycolic acid of 70 percent strength, that is, 70 percent of glycolic acid and a balance of water, and 0.5 mole of 37.3 percent strength hydrochloric acid which is 37.3 percent by weight HCl in water. The container is covered and good ventilation is provided. After the ingredients are placed together in the container, dissolution of the chromium starts slowly but gradually increases thus supplying heat to the reaction. As the reaction continues the temperature of the reaction medium reaches 71°C. without external heating and the chromium metal can be seen by visual inspection to be substantially dissolved. As the temperature starts to subside from 71°C., external heating is applied and the temperature of the reaction medium is permitted to reach 88°C. until all the chromium is dissolved. Total reaction time i.e., to complete chromium metal dissolution, is about 4 hours. Thereupon the solution is heated at reflux, reaching a temperature of 107°C., for about 2 hours, and is thereafter permitted to cool.

The resulting complex, having a molar ratio of chromium to glycolic acid of 1:2.25 and of chromium to chloride of 1:0.625, is added to water to provide a concentration of chromium metal of 40 grams per liter (g./l.). To this added 150 g./l. of KCl and 63 g./l. of H_3BO_3. The pH of the bath is adjusted to 2.94 by the addition of 40 percent strength sodium hydroxide, that is, 40 weight percent NaOH in a balance of water, and the final volume of the bat is adjusted to 1,000 milliliters (mls.) by subsequent addition of water.

The bath is electrolyzed for 10 to 20 amp hrs./gal. and is then ready for plating in the above-described modified Hull cell. In the Hull cell graphite anodes are used and the cathode for the test is a 3 15/16 inches × 2 ⅝inches brass panel, each panel being nickel coated prior to use in the cell. The test is carried out using 10 amperes current for a 3 minute cycle at 12.5 volts and the bath temperature is maintained at 87°F. In this plating test the bright range extended from 800 ASF to 6 ASF at the high and low current density areas respectively. Over the plating range the plate exhibits a reflective reflectance value of 50 percent, with the color of the chromium deposit being of a slightly darker cast than that observed with commercially available decorative chromium deposits from hexavalent chromium plating baths, the deposit thus exhibiting a deep and rich appearance. The results from this bath have been plotted as the upper graph line in the drawing.

EXAMPLE 2

In the manner of Example 1 there is placed sufficient chromium metal, together with sufficient 88.4 percent strength lactic acid, that is, 88.4 percent lactic acid and the balance water, together with an amount of 37.3 percent strength hydrochloric acid, to provide a mole ratio of chromium to lactic acid of 1:1.625 and a mole ratio of chromium to chloride of 1:0.625. The contents of the container are reacted in the manner of Example 1, i.e., are permitted to react without external heating, followed by external heating and subsequently by refluxing.

Upon cooling, a portion of the resulting solution in an amount sufficient to provide 40 grams of chromium per liter, is blended with about 150 g./l. potassium chloride, and about 60 g./l. H_3BO_3, and the bath is maintained at a pH of 2.94–3.0 by the addition of 40 percent strength sodium hydroxide. Plating tests, conducted in the manner of Example 1, after electrolyzing the bath as described in Example 1, are carried out using the Hull cell with graphite anodes and the nickel plated panel cathodes, and using 10 amperes of current for a 3 minute cycle at 13.5–14.0 volts and with the bath temperature maintained between 87°–96°F. From these tests, the bright range can be seen to extend completely across the panels, representing a range of approximately 1,000 to 1 ASF which is unique in the history of decorative chromium plating. The showing of a definite chromium thickness at the 5 ASF current density level of as high as 1.7 micro-inches per 3 minute cycle is regarded as an indication that the bath prepared in this Example will still deposit chromium at the 1–2 ASF level.

EXAMPLE 3

In the manner of Example 1, sufficient chromium metal, along with a sufficient amount of oxalic acid plus 37.3 percent strength hydrochloric acid to provide a molar ratio of chromium to oxalic acid of 1:1.8 and a molar ratio of chromium to chloride of 1:0.625, are placed in a reaction vessel. Reaction proceeds in the manner of Example 1, e.g., initially without external heating and finally with refluxing. Bath preparation is completed by adding this complex to water to provide a concentration of 40 grams of chromium per liter of the bath, and further admixing therewith about 150 g./l. of potassium chloride and about 60 g./l. of H_3BO_3. In the manner of Example 1, the pH of the bath is adjusted to 3.0 by the addition of sodium hydroxide, and water is added to bring the final volume of the bath to 1,000 mls.

Plating tests are carried out in the manner of Example 1 with the bath temperature being deliberately varied to show effect on plating results. The bright range for a test at 92°F., is from 400 ASF down to 7 ASF, and the bright range for a test at 105°F. is measured from 450 ASF down to 9 ASF. Further, the chromium plating on the nickel plated panel cathodes for each test is seen by visual observation to have the same finish as that described for the chromium plating in the tests of Example 1.

EXAMPLE 4

Into a reaction vessel containing 400 mls. of water there is dissolved 210 grams of chromium fluoride ($CrF_3 \cdot 9H_2O$) and to this is added 153 mls. of the 70 percent strength glycolic acid of Example 1. While this mixture is constantly agitated there is gradually added thereto 70 grams of potassium hydroxide. During addition of the potassium hydroxide, the reaction is exothermic and, as agitation in the mixture is continued, external heating is applied until the mixture is brought to boiling and is refluxed for several hours. Following this the volume of the mixture is adjusted to 750 mls. by the addition of water and to this there is added 56.6 grams of H_3BO_3 and 150 grams of potassium chloride, with agitation. As the mixture is further permitted to cool to 90°F., the volume is adjusted to 1 liter and the pH is adjusted to 3.4 in the manner of Example 1.

The resulting bath contains sufficient complex to provide 40 grams of chromium per litter of the bath and the complex has a molar ratio of chromium to glycolic acid of 1:2.25 and of chromium to fluoride of 1:3. Thereafter the bath is electrolyzed for 0.5 hour at a current of 12 amperes. Plating tests are carried out in the manner of Example 1 and give a full bright range coverage to the extreme low current density end of the panel and lacked 2 percent coverage at the extreme high current density area. The bright range is then deemed to be from about 950 ASF down to 1–2 ASF. The finish on the panel is comparable to the finish described in the panels plated in Example 1, i.e., the panel has a reflective reflectance value of 50 percent, has a desirably rich and deep appearance, and the color of the chromium deposit is of a slightly darker cast than that observed with commercially available decorative chromium deposits from hexavalent chromium plating baths.

EXAMPLE 5

For comparative purposes only, i.e., to compare the methods of preparation of the present invention with a bath similarly prepared, a comparative chromium glycolate complex is prepared in accordance with the precepts of U. S. Pat. No. 3,006,823. For this, there is added to a reaction vessel containing 3,000 mls. water, 4,398 grams glycolic acid. This mixture is heated to 70°C. and is then gradually combined with a solution of chromic acid containing 2,700 grams chromium, expressed as CrO_3, and 1,680 mls. water. During the slow addition of the chromic acid solution, the temperature in the reaction medium is maintained at 70°C. After addition of the chromic acid solution, the reaction mixture is heated to 90°C. and held at that temperature for 1 hour. Subsequently, the mixture is permitted to cool and is diluted with water to 11,232 mls.

A portion of this resulting solution sufficient to provide a chromium concentration of 52 g./l. is blended with 150 g./l. potassium chloride, 62 g./l. of H_3BO_3, and 86 mls. per liter of glycolic acid of 70 percent strength. The pH of this bath is adjusted in the manner of Example 1 to a pH of about 3 and the bath is electrolyzed to prepare same for evaluation of plating performance.

Using the Hull cell as above described, a plating test is run on this comparative bath in the manner of Example 1, i.e., a nickel plated brass panel cathode is employed and the bath is operated using 10 amperes current for a 3 minute cycle. The results of such test are plotted in the drawing and form the lower line appearing on the graph of the drawing. By reference to such drawing, the superior performance obtained by the bath of the present invention compared to this comparative bath of Example 5, is readily evidenced.

I claim:

1. The method of preparing an aqueous electrolytic plating bath for the plating of bright chromium plate from trivalent chromic-compound which method comprises:

   1. establishing an aqueous medium containing a complex, water-soluble chromic compound containing halogen constituents selected from the group consisting of chloride, fluoride, mixtures thereof and mixtures thereof with other halides, and said chromic compound containing carboxylic acid constituents supplied by acids selected from the group consisting of glycolate, lactate oxylate and mixtures thereof, with said compound supplying not substantially above about 150 grams of chromium per liter of the medium, said complex having a molar ratio of chromium atoms to carboxyl constituent within the range of 1:0.7 to 1:3, and a molar ratio of chromium atoms to halogen atoms within the range of 1:0.1 to 1:3.5;
   2. adjusting the pH of said medium within a range of between about 1.8 and about 4.9; while
   3. maintaining the temperature of said medium not substantially in excess of about 50°C.

2. The method of claim 1 wherein said medium is furnished with between about 10–70 grams per liter of substance selected from the group consisting of boric acid, a substance supplying boric acid equivalent in aqueous solution, and mixtures thereof.

3. The method of claim 1 wherein said medium is furnished with between about 50–200 grams per liter of a salt of a strong acid having a dissociation constant of at least $K=10^{-2}$.

4. The method of preparing an aqueous electrolytic plating bath for the plating of bright chromium plate from trivalent-chromic compound, which method comprises:

1. establishing a liquid, aqueous reaction medium containing chromium metal, carboxylic acid supplied by acids selected from the group consisting of glycolate, lactate, oxalate and mixtures thereof, and halogen providing compound containing halogen constituents selected from the group consisting of chloride, fluoride, mixtures thereof and mixtures thereof with other halide, and with sufficient of said carboxylic acid to provide said medium with a molar ratio of total chromium atoms to total acido groups within the range of 1:0.7 to 1:3, and with sufficient halogen-providing compound to supply said reaction medium with a molar ratio of total chromium atoms to total halogen atoms within the range of 1:0.1 to 1:3.5;
2. permitting reaction of the substituents in said medium, thereby preparing therein a complex, water-soluble trivalent chromic compound containing carboxylic acid constituents and halogen constituents;
3. adjusting the concentration of said complex in said medium to supply not substantially above about 150 grams of chromium per liter of the medium;
4. adjusting the pH of said medium within a range of between about 1.8 and about 4.9; and
5. maintaining the temperature of said medium below about 50°C.

5. The process of claim 4 wherein said halogen providing compound is selected from the group consisting of hydrogen fluoride, sodium fluosilicate, fluorine gas, hydrogen chloride, chlorine gas, and mixtures thereof.

6. The method of claim 4 wherein said medium is furnished with between about 10–70 grams per liter of substance selected from the group consisting of boric acid, a substance supplying boric acid equivalent in aqueous solution, and mixtures thereof.

7. The method of claim 4 wherein said medium is furnished with between about 50–200 grams per liter of a salt of a strong acid having a dissociation constant of at least $K=10^{-2}$.

8. The process of claim 4 wherein water supplies all of the liquid of said reaction medium, such medium is heated to boiling during reaction, and said chromium metal is in pulverulent form.

9. The process of preparing an aqueous electrolytic plating bath for the plating of bright chromium plate from trivalent-chromic compound, which process comprises:

1. bringing together in a liquid reaction medium, chromic acid, carboxylic acid supplied by acids selected from the group consisting of glycolate, lactate, oxalate and mixtures thereof, and halogen-providing compound containing halogen constituents selected from the group consisting of chloride, fluoride, mixtures thereof and mixtures thereof with other halide, with sufficient of said carboxylic acid to provide said medium with a molar ratio of total chromium atoms to total acido groups within the range of 1:0.7 to 1:3, and with a halogen-providing compound sufficient to supply said medium with a molar ration of total chromium atoms to total halogen atoms within the range of 1:0.1 to 1:3.5;
2. permitting reaction of the substituents in said medium, thereby preparing therein a complex water-soluble trivalent chromic compound containing carboxylic acid constituents and halogen constituents;
3. adjusting the concentration of said complex in said medium to supply not substantially above about 150 grams of chromium per liter of the medium;
4. adjusting the pH of said medium within a range of between about 1.8 and about 4.9; and
5. maintaining the temperature of said medium below about 50°C.

10. The process of claim 9 further characterized by a liquid reaction medium containing fugitive liquid that is at least substantially volatized after preparation of said complex.

11. The process of claim 9 wherein said halogen-providing compound is selected from the group consisting of hydrogen fluoride, sodium fluosilicate, fluorine gas, hydrogen chloride, chlorine gas, and mixtures thereof.

12. The method of claim 9 wherein said medium is furnished with between about 10–70 grams per liter of substance selected from the group consisting of boric acid, a substance supplying boric acid equivalent in aqueous solution, and mixtures thereof.

13. The method of claim 9 wherein said medium is furnished with between about 50–200 grams per liter of a salt of a strong acid having a dissociation constant of at least $K=10^{-2}$.

14. The process of preparing an aqueous electrolytic plating bath for the plating of bright chromium plate from trivalent chromic compound, which process comprises:

1. establishing a liquid, aqueous reaction medium comprising chromium-providing material selected from the group consisting of chromic halide, basic chromic halide, and mixtures thereof supplying halide constituents selected from the group consisting of chloride, fluoride, mixtures thereof and mixtures thereof with other halide, said chromium-providing material being in mixture with carboxylic acid selected from the group consisting of glycolate, lactate, oxalate, and mixtures thereof, said acid being in amounts sufficient to provide said medium with a molar ratio of total chromium atoms to total acido groups within the range of 1:0.7 to 1:3;
2. permitting reaction of the substituents in said medium, thereby preparing therein a complex, water-soluble trivalent chromic compound containing carboxylic acid constituents and halogen constituents;
3. adjusting the concentration of said complex in said medium to supply not substantially above about 150 grams of chromium per liter of the medium;
4. adjusting the pH of sad medium within a range of between about 1.8 and about 4.9; and

5. maintaining the temperature of said medium below about 50°C.

15 The process of claim **14** wherein said reaction medium additionally contains a strong base yielding hydroxyl ions in said aqueous reaction medium when said chromic halide is present.

16. The method of claim **14** wherein said medium is furnished with between about 10–70 grams per liter of substance selected from the group consisting of boric acid, a substance supplying boric acid equivalent in aqueous solution, and mixtures thereof.

17. The method of claim **14** wherein said medium is furnished with between about 50–200 grams per liter of a salt of a strong acid having a dissociation constant of at least $K=10^{-2}$.

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