

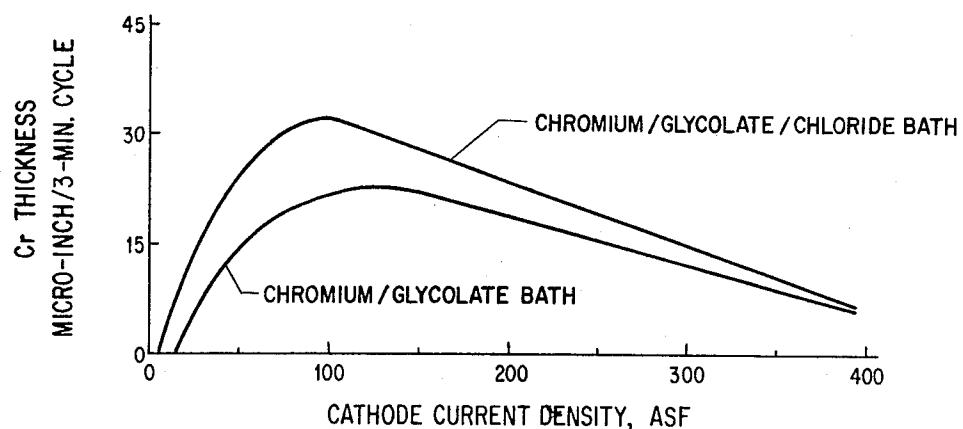
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CHROMIUM PLATING BATH CONTAINING CHROMIC COMPOUND

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CHROMIUM PLATING BATH CONTAINING CHROMIC COMPOUND

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13 Claims

ABSTRACT OF THE DISCLOSURE

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

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 provide 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. 3,066,823 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 invention is directed to an aqueous electrolytic plating medium comprising a complex, water-soluble chromic compound containing carboxylic acid constituents and halogen constituent selected from the group consisting of chlorine, fluorine, bromine, iodine or mixtures thereof, with the medium having a molar concentration of chromium within the range from about 0.5 to about 3.

The invention is further directed to a method of chromium plating an article with bright chromium plate using the medium of the present invention and further to the chromium plated article thereby obtained. The present invention is still further directed to an additive concentrate for preparing or sustaining a chromium plating bath, such concentrate comprising the above-described water-soluble complex.

BRIEF DESCRIPTION OF THE DRAWING

The drawing presents in graphic form and for comparative purposes, thickness of chromium deposit for a bath of 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 bath of 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 micro-inches for a three minute plating cycle using 10 amperes of current in a

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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 of the present invention 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. 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 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 for the complex. The carboxylic acid constituent of 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 such as those discussed in more detail hereinbelow whereby the complex is formed, in the same manner as the free acid, can be used.

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.

The complex can be prepared by any of several methods, and representative methods are discussed herein, but should not be construed as being exhaustive. One method is the straightforward combination of chromium metal with carboxylic acid plus, 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, where the reaction proceeds in a liquid medium such as an aqueous medium such external heating can involve refluxing of the reaction mixture to augment completion of the reaction.

The complex may also be prepared from the carboxylic and hydrochloric acid in admixture with chromic acid, typically charged to the reaction medium as a solution of chromic acid in water. 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. The complex may further be prepared by reaction of chromic halide, 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. For example, $\text{CrF}_3 \cdot 9\text{H}_2\text{O}$ may be used in this method and will readily yield a chromium/carboxylic acid/fluoride complex involving exothermic reaction conditions.

The complex is present in 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 the 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 present 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 contain 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 contain boric acid, or an equivalent to boric acid in aqueous solution, such as borax, boron oxide, or sodium oxyfluoroborate. 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.

Such a salt of a strong acid, alone or along with boric acid or boric acid equivalent, can also be blended into a solution for use in establishing or sustaining a plating bath. Typically, when the complex is prepared, as by the above described methods, the amount of complex in the freshly prepared solution supplies above about 50 grams of chromium per liter of the solution. More often, such fresh solutions contain sufficient complex to provide greater than 75 grams, e.g., 100-150 grams, of chromium per liter. These solutions can be stored and then subsequently used for preparing a new bath, or for sustaining a working bath, as such baths typically contain an amount

of complex providing from about 25 to about 75 grams of chromium per liter.

These freshly prepared concentrated solutions may be blended before storage with sufficient salt of a strong acid to prepare a solution having a molar ratio of moles of chromium, supplied by the complex, to moles of salt of a strong acid, of between about 1:1.5 to 1:2.5. Moreover, the freshly prepared solution either alone, or blended with salt of a strong acid, may be blended before storage with sufficient boric acid or boric acid equivalent to supply the blend with a molar ratio of moles of chromium provided by the complex to moles of boric acid equivalent of between about 1:1.1 to about 1:0.3. These solutions may then be stored, or directly used, e.g., in a working bath, to supply complex for replenishment of chromium and to supply the salt of a strong acid and/or boric acid to replenish the losses of these materials that can occur, for example through drag-out. Stored solutions may thereafter find particular use, as in enhancing conductivity and augmenting rate of deposition of chromium, in chromium plating baths and especially in baths containing trivalent chromium in complex form that are employed for the deposition of bright, decorative chromium plate.

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.

During plating, 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. During plating, a desirable, bright decorative chromium plate of commercially acceptable thickness can typically be plated from about 1000 a.s.f. down to about 3 a.s.f. during a three minute plating cycle. Such bright plating range is unique in the history of decorative chromium plating.

When the substrate to be plated is immersed in the plating bath, care should be taken that the surface for deposition is fully wetted by the plating bath prior to current flow. In such operation where the substrate to be plated is immersed in the plating bath, typical operation provides for passage of current not substantially longer than about seven minutes, yielding a chromium deposit on the cathode surface having a thickness not substantially above about 0.0002 inch. 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 substrate which may be employed for receiving the decorative-protective finish provided by the chromium plate of the present invention includes metals such as steel, brass, copper, copper alloys, bronze, zinc diecastings, as for example to prevent rusting or tarnishing, or nickel surfaces. Additionally such plating can be performed on plastic surfaces which are activated or prepared for an electroplating operation. The plating can be typically 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. Also, electrodeposition with the plating composition can be performed in the bath by any conventional plating

technique including rotating receptacle coating apparatus immersed in the plating bath. Further the method is applicable to the plating of substrates by the use of portable plating devices wherein the apparatus supplies the electrolyte and a positive source of electrical current, e.g., brush or stylus means for applying the plating composition to a substrate. Although diaphragm compartment cells may be employed for plating, they are not preferred for economy.

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. 2,149,344. 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 $A = C(27.7 - 48.7 \log L)$ wherein A is the current density in amps per square foot (a.s.f.) 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, $\frac{1}{2}$ -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 moles of glycolic acid of 70% strength, that is, 70% of glycolic acid and a balance of water, and 0.5 mole of 37.3% strength hydrochloric acid which is 37.3% 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 is 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% strength sodium hydroxide, that is, 40 weight percent NaOH in a balance of water, and the final volume of the bath is adjusted to 1000 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 each test is a $3\frac{13}{16}'' \times 2\frac{5}{8}''$ brass panel, each panel being nickel coated prior to use in the cell. Each test is carried out using 10 amperes current for a 3 minute cycle. The results shown in the table below give the rates of deposition at seven specific current density levels. The chromium thickness reported at each density level is in micro-inches per 3 minute cycle. The cur-

rent density range shown in the table is in amperes per square foot (a.s.f.).

TABLE 1

Bath pH	Bath temp., °F.	Volts	Current density range (a.s.f.)						
			400	300	200	100	40	20	10
2.0	87	12.5	7	15	24	33	19	8	4
2.9	87	12.5	8	12	18	24	17	7	4

In this plating test the bright range extended from 800 a.s.f. to 6 a.s.f. 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 the fresh bath, i.e., the results first given in the table, 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% strength lactic acid, that is, 88.4% lactic acid and the balance water, together with an amount, of 37.3% 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 initially adjusted to a pH 2.94 by the addition of 40% strength sodium hydroxide. Subsequently, as shown in the table below, additional adjustment of the pH is made during plating tests by further addition of sodium hydroxide solution.

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. The results given in the table below are for eight different specific current density levels, and are in chromium thickness reported in micro-inches per 3 minute cycle at current density ranges in a.s.f.

TABLE 2

Bath pH	Bath temp., °F.	Volts	Current density range (a.s.f.)						
			400	300	200	100	40	20	10
2.94	87	13.5	9	4	4	11	10	8	5.5
3.0	90	14.0	9	4	5	13	13	9	6
3.0	96	13.5	6	5	7	19	13	9	4
									0.8

NOTE.—N.M.=Not measurable.

The bright range for some panels from this test extends completely across the panels, representing a range of approximately 1000 to 1 a.s.f. which is unique in the history of decorative chromium plating. The showing of a definite chromium thickness at the 5 a.s.f. current density level is regarded as an indication that the system will still deposit chromium at the 1-2 a.s.f. level.

EXAMPLE 3

In the manner of Example 1, sufficient chromium metal, along with a sufficient amount of oxalic acid plus 37.3% 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.

A bath is prepared 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 1000 mls.

Plating tests are carried out in the manner of Example 1 and the results are reported in the table below in the manner of Example 1. Variation in the bath temperature as shown in the table below is deliberate to show affect on plating results.

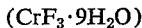
TABLE 3

Bath pH	Bath temp., °F.	Volts	Current density range (a.s.f.)				
			300	200	100	40	20
3.0-----	92	12.5	17	24	20	7	4
3.0-----	105	11.3	8	16	13	4	3

The bright range for the initial test, i.e., for the test at 92° F., is from 400 a.s.f. down to 7 a.s.f., and the bright range for the test at 105° F. is measured from 450 a.s.f. down to 9 a.s.f. 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



and to this is added 153 mls. of the 70% 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 liter 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 the results are reported in the table below in the manner of Example 1.

TABLE 4

Bath pH	Bath temp., °F.	Volts	Current density range (a.s.f.)					
			300	200	100	40	20	10
3.4-----	97	14.0	20	29	32	12	7	4 1.6

The plating test gives a full bright range coverage to the extreme low current density end of the panel and lacked 2% coverage at the extreme high current density area. The bright range is then deemed to be from about 950 a.s.f. down to 1-2 a.s.f. 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%, 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

bath of the present invention with a similar bath, a comparative chromium glycolate complex is prepared in accordance with the precepts of U.S. Pat. 3,006,823. For this, there is added to a reaction vessel containing 3000 mls. water, 4398 grams glycolic acid. This mixture is heated to 70° C. and is then gradually combined with a solution of chromic acid containing 2700 grams chromium, expressed as CrO_3 , and 1680 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 one 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% 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, as rates of deposition at seven different specific current density levels, are shown in the table below for a freshly prepared bath.

TABLE 5

Bath pH	Current density range (a.s.f.)				
	400	200	100	40	20
3.0-----	7	20	21	12	4

These results as shown in the table are plotted in the drawing and form a part of the lower line appearing on the graph of the drawing. By reference to such drawing and to Example 1, the superior performance obtained by the bath of the present invention compared to this comparative bath of Example 5, is readily evidenced.

What is claimed is:

1. An aqueous electrolytic plating medium for the plating of bright chromium plate said medium comprising a complex, water-soluble trivalent chromic compound containing halogen constituents selected from the group consisting of chloride, fluoride, mixtures thereof and mixtures thereof with other halide, and said complex containing carboxylic acid constituents supplied by acids selected from the group consisting of glycolate, lactate, oxalate, and mixtures thereof, said medium having a molar concentration of chromium within the range from about 0.5 to about 3 and 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. The medium of claim 1 wherein said halogen is selected from the group consisting of fluoride and mixtures thereof with other halides.

3. The medium of claim 1 wherein said medium is maintained within a pH of between about 1.8-4.9 and at a temperature not substantially above about 50° C.

4. The medium of claim 1 wherein articles to be plated are immersed therein and said complex is present in said medium in an amount supplying not substantially above about 75 grams of chromium per liter of the medium.

5. The medium of claim 1 and additionally containing a salt of a strong acid having a dissociation constant of at least $K=10^{-2}$, and a substance selected from the group consisting of boric acid, a substance supplying boric acid equivalent in aqueous solution, and mixtures thereof.

6. The medium of claim 5 wherein the cation of said salt is selected from the group consisting of sodium, potassium, and their mixtures, and the anion of said salt is

chloride, and said bath contains between about 50-200 grams per liter of said salt.

7. The medium of claim 5 wherein said substance supplying boric acid equivalent in aqueous solution is selected from the group consisting of borax, boron oxide, sodium oxyfluoborate, and mixtures thereof and said medium contains between about 10-70 grams per liter of said substance.

8. The method of plating an article with bright chromium plate comprising passing an electrical current between an anode and an article forming a cathode which are in contact with an aqueous chromium plating medium comprising a complex, water-soluble trivalent chromic compound containing halogen constituents selected from the group consisting of chlorine, fluorine, mixtures thereof, and mixtures thereof with other halide, and said complex containing carboxylic acid constituents supplied by acids selected from the group consisting of glycolate lactate, oxalate, and mixtures thereof, said medium having a molar concentration of chromium within the range from about 0.5 to about 3, and 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.

9. The method of claim 8 wherein during passage of said current said bath is maintained at a pH between about 1.8-4.9 and at a temperature not substantially above about 50° C.

10. A chromium plating solution for dilution with aqueous medium in preparation of a plating bath for the plating of bright chromium plate upon articles immersed therein, said solution containing, in aqueous medium, the trivalent-chromium-containing reaction complex from halogen, carboxylic acid, and chromium-providing substance, said plating solution comprising a con-

centrate in water medium of said complex supplying above about 50 grams of chromium per liter of the medium, said complex containing halogen constituents selected from the group consisting of chlorine, fluorine, mixtures thereof, and mixtures thereof with other halide, and said complex containing carboxylic acid constituents supplied by acids selected from the group consisting of glycolate, lactate, oxalate, and mixtures thereof, 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.

11. The plating solution of claim 10 wherein said halogen constituent is selected from the group consisting of fluoride and mixtures thereof with other halides.

12. The plating solution of claim 10 characterized by containing a molar ratio of moles of chromium supplied by said complex to moles of a salt of a strong acid having a dissociation constant of at least $K=10^{-2}$, of between about 1:1.5 to 1:2.5.

13. The plating solution of claim 10 characterized by containing a molar ratio of moles of chromium supplied by said complex to moles of boric acid equivalent of between about 1:1.1 to about 1:0.3.

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