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CHROMIUM PLATING WITH CHROMIC COMPOUND AND ORGANIC ADDITIVE

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ABSTRACT OF THE DISCLOSURE

Deposition of bright decorative chromium plate with a chromium plating medium containing trivalent chromic compound is enhanced in the high current density area by addition to the medium of a minor amount of an organic additive. Such media most typically contain a chromic-compound also having at least carboxylic acid constituents and further exhibiting ready water solubility. The organic additives employed will enhance the chromium rate of deposition from such baths in the high current density area as well as plate thickness without deleterious effect to plating characteristics at the low current density region. Typically, only very minor amounts of polar aprotic substances and ethers and thioethers will provide such effect.

BACKGROUND OF THE INVENTION

Decorative chromium plating from baths containing chromium in the trivalent state in association with at least carboxylic acid constituents has offered promise for commercial use; U.S. Pat. No. 3,006,823, for example, describes a recently developed aqueous electrolytic plating bath containing a chromium complex of chromic ion and carboxylic acid. However, in working such baths, desirable performance in chromium rate of deposition in the high current density area is not always achieved for an extended period. Undesirable plate may be experienced in the high current density region, not only for plating thickness, but also with regard to the extent or range over which an acceptable plate thickness can be attained.

SUMMARY OF THE INVENTION

Decorative chromium plating baths containing trivalent chromic compound in association with at least carboxylic acid constituents now will show enhanced deposition in the high current density area, both in acceptable plating thickness and in the range of such thickness within the region, by addition to the bath of very minor amounts of organic additives. Further the addition of such additives does not provide for deleterious effect on low current density area plating characteristics thus further enhancing the commercial potential of such baths.

Broadly, the invention is directed to aqueous electrolytic plating baths for the plating of bright chromium plate and that exhibit enhanced electrodeposition of such plate; more particularly, such baths comprise a complex, water-soluble chromic compound for the deposition of the chromium plate and an organic component. This organic component is composed of at least one compound of: (1) polar aprotic substances; and, (2) cyclic and acyclic ethers and thioethers; as well as mixtures of any of such organic materials.

More particularly the polar aprotic substances are selected from the group consisting of tetrahydrothiophene-1,1-dioxide, dimethyl formamide, N-methylpyrrolidone, dimethylsulfoxide, dimethylsulphone, and mixtures thereof and ring substituted derivatives of such substances that are cyclic dipolar substances having ring substituents other than hydrogen. The substituents can be the same or different and are selected from the group consisting of hydroxyl, lower alkyl, lower alkoxy, hydroxyalkyl, and dialkylamino, with there being less than four ring carbon atoms having the substituents. The cyclic and acylic ethers and thioethers have an atomic ratio of oxygen atoms, or sulfur atoms, or both, to carbon atoms of greater than 0.25:1 and below 0.9:1.

The invention is further directed to the method of chromium plating an article with a decorative chromium plate from a medium showing enhanced deposition in the high current density area and is also directed to the method of enhancing such electrodeposition of bright chromium plate from an aqueous chromium plating medium containing water-soluble chromic plating compound.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The chromic compound can typically contain carboxylic acid constituent, e.g., be provided by the chromic carboxylate of the aqueous electrolytic plating baths disclosed in U.S. Pat. No. 3,006,823. As taught therein, the chromic compound is preferably a chromic carboxylate of an alpha-hydroxy carboxylic acid, for example glycolic and lactic acids, although other acids can be employed such as will be discussed more particularly hereinbelow. The carboxylates may be added to the plating bath as such or, as taught in U.S. Pat. No. 3,021,267, they may be provided by dissolving chromic hydroxide or carbonate or even metallic chromium in the carboxylic acid and the pH adjusted with sodium hydroxide or carbonate. As used herein the term "chromic carboxylate" is meant to refer to such compounds of trivalent chromium and carboxylic acid as are exemplified by such patents.

The bath for the electrodeposition of bright chromium plate may also contain a water-soluble chromic compound containing carboxylic acid constituents plus halogen constituents which can be chlorine, fluorine, bromine, iodine, or mixtures thereof. However, in typical plating operation the bromine and iodine may lead to evolution of visible noxious fumes at the anode. Therefore, chlorine and fluorine are almost exclusively used. The carboxylic acid constituent is most typically supplied by a non-aromatic carboxylic acid having less than about ten carbon atoms and being free from carbon-to-carbon unsaturation, which acid is a dicarboxylic acid, or a monocarboxylic acid, or such acids having at least one hydroxyl group, or mixtures of such acids.

Representative acids which can or have been used in such above discussed chromic compounds include glycolic acid, lactic acid, oxalic acid, and their mixtures. Preferably, for enhanced plating performance, plus economy, although it is not meant that this invention be bound to baths wherein the chromic compound contains only carboxylic acid constituents above, the baths used virtually always contain a chromic compound which has carboxylic acid constituents supplied at least in part by glycolic acid. A compound or any of these acids such as a salt or an ester thereof, which acts 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.

In preparing a plating bath containing a chromic carboxylate, typically chromic acid can be reacted with the carboxylic acid. For example, to reduce one mole of the chromic acid, 0.5 mole of glycolic acid may be used and 1.0 mole of glycolic acid is generally present to form the desired complex. Typically excess acid, e.g., a 0.1 mole excess, is present to insure reduction and complex formation. Thus, more particularly, chromic acid present as a solution in water, may be slowly added to glycolic acid, also dissolved in water, at 90–100° C. When addition is complete, the solution can be heated to reflux and typically maintained at reflux for about one hour or more to complete reaction.

When halogen is incorporated in the complex, the complex can be prepared by any of several methods. One method is the straightforward combination of chromium metal with carboxylic acid plus 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 aqueous medium such external heating can involve refluxing of the reaction mixture to augment completion of the reaction.

The complex of this type may also be prepared from the carboxylic acid 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. These complexes may further be prepared by reaction of chromic halide, with such halide corresponding to the halide that is to be present in the complex; the chromic halide is reacted with the carboxylic acid, with this reaction further involving the addition of strong base, e.g., an alkali metal hydroxide. 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.

These carboxyl containing complexes virtually always contain a molar ratio of chromium atoms to carboxylate constituent within the range of 1:0.7 to 1:3.0. Where halogen is present the complex essentially always has 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 plating performance and economy can depend upon the acid and also upon the halogen constituent when such is present. Thus for example, for a chromic carboxylate prepared with glycolic acid, the ratio of the chromic ion to glycolic is preferably maintained within the range from about 1:1.1 to 1:2.1. For a complex containing a substantial amount of the glycolic acid for the carboxylate, which complex further contains chloride as the major amount, to all, of the halogen, the 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 ratio of chromium atoms to halogen is preferably within the range of 1:2.6 to 1:3.2.

The complex is generally present in the bath 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 generally within the range from about 0.5 to about 3.0, although for the baths containing chromic carboxylate as little as 0.1 mole of chromium in the plating medium is serviceable. The more highly concentrated baths having augmented viscosity are not well suited for deposition of chromium onto a substrate immersed therein. Thus such baths having molar concentration of chromium above about 1.5 are typically used in portable plating devices for spot plating, e.g., brush plating. Regardless of plating method, the bath is one where the complex is present in a liquid medium supplied preponderantly by water, e.g., such medium will also have a very minor contribution from the organic additives when they are in a liquid form and may contain carboxylic acid, e.g., as taught in U.S. Pat. No. 3,021,267.

The organic component for the bath can be one or more substances which are water soluble or readily miscible with water and are often materials that are liquid at normal pressure and temperatures. Substances which are not soluble or readily miscible with water can be difficult to readily disperse in the bath and are thus avoided. For addition to the bath, the organic component can be added in any convenient manner, for example as a water dispersion or as a blend in solution with chromic compound; such a blend may then be used in preparing fresh baths or for replenishing a bath during working. The liquid organic component is used in the bath in an amount not generally exceeding about 5 volume percent, basis total volume of the bath. Addition of greater than about 5 volume percent of such substances will typically not offer any significant enhancement in extending the high current density range and may deleteriously affect the low current density plating range. Usually for desirable enhancement in the high current density range the additive is present in a concentration of greater than about 0.1 volume percent basis total volume of the bath and preferably for economy and such enhancement the organic additive is present in amount between about 1.5–3 volume percent. Where the additive is in solid form when added to the bath, it is advantageously, for economy, added in an amount not exceeding above about 5 weight percent, basis total weight of the bath.

The organic component can be contributed by polar aprotic substances that may be cyclic or acyclic organic materials or their mixtures. For the cyclic polar aprotic compounds less than four ring carbon atoms can have substituents other than hydrogen. Such substituents may be the same or different and may be hydroxyl, lower alkyl, lower alkoxy, hydroxy alkyl, or dialkylamino. Generally for economy and efficiency the lower alkyl, for example, refers to constituents containing less than four carbon atoms. Polar aprotic substances which may be or have been used include tetrahydrothiophene-1,1-dioxide, dimethyl formamide, N-methylpyrrolidone, dimethylsulfoxide, dimethylsulfone, and mixtures thereof.

Additional organic substances which can make up or contribute to the organic component are cyclic and acyclic ethers and thioethers. For most desirably enhancing the extension of the high current density region, the compounds of this group should have an atomic ratio of oxygen atoms, or sulfur atoms, or both, to carbon atoms of greater than 0.25:1 and below 0.9:1. Most generally, these compounds have such a ratio of from about 0.3:1 to about 0.7:1. Additionally these compounds may contain hydroxyl groups, e.g., as with the cyclic ether tetrahydrofurfuryl alcohol, but for efficiency and economy should not have more than three hydroxyl groups and have a molar ratio of hydroxyl groups to oxygen atoms, or sulfur, or both, of not above 3:1. Such compounds bearing carboxyl groups should have not more than two carboxyl groups and have a molar ratio of this group to oxygen and the like of not above 1:1. Representative cyclic and acyclic ethers and thioethers in addition to such as have already been mentioned include bis(2-methoxyethyl)ether, diethylene glycol monomethyl ether, 1-(2-methoxypropoxy) - 2 - propanol, dipropylene glycol, tetrahydrofuran, tetraethylene glycol, vinyl sulfide, butoxytriglycol, and their mixtures.

Of particular interest in the baths containing the organic component, and thus exhibiting enhanced chromium deposition at the high current density area without deleterious effect at the low current density region, is the throwing power performance. Such performance can be expressed as a ratio of deposit thickness in the high current density region, e.g., 400 amperes per square foot (ASF), to the deposit thickness in the low current density area, such as 40 ASF. Typically, commercially available hexavalent-chromium-containing baths for the deposition of bright chromium plate will show a ratio of 12:1 with the thickness being checked at 400 ASF and 40 ASF. For the trivalent chromium baths containing organic component, some may show even distribution of chromium thickness to have a throwing power ratio between 400–40 ASF of 1:2.

Although particular baths may contain certain specified additional substances and in particular amounts, e.g., the amounts of free carboxylic acids called for in the bath of U.S. Pat. No. 3,021,267, in general 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, perchlorate, or 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 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 both.

Before deposition of chromium, the bath pH is adjusted to within a range depending upon the complex present, e.g., for a bath containing a major amount of just one chromic carboxylate the bath is adjusted to a pH within the range from about 1.5–3.0. For a bath wherein the major amount of complex is contributed by such substance further containing halogen atoms the bath is adjusted to a pH within the range from about 1.8 to 4.9. For these latter baths the most desirable pH range is generally between about 2.0–3.5 and can depend upon the make-up of the complex present in the plating medium with, for example, a complex containing a substantial amount of fluorine as the halogen being preferably maintained at a slightly more elevated bath pH than for a bath where chlorine supplies the major amount of the halogen. 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 bath, such material for adjusting the bath pH can be initially dissolved in water and the water solution then added to the bath.

The temperature of the bath during plating, for efficiency and economy is in part dependent upon the complex present in the bath with such baths as contain a major amount of chromic carboxylate typically being maintained during plating at a temperature within the range from room temperature up to about 90° C., but more typically up to about 65° C. For those baths where the major amount of the complex contains a halogen, the temperature is advantageously for enhanced plating performance not substantially above about 50° C.

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. Exemplary cathode substrates for receiving the plate include metal such as steel, brass, copper, copper alloys, bronze, zinc die castings, and nickel. 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 such plating baths containing their organic additives can be performed by any conventional plating technique including rotating receptacle coating apparatus immersed in the plating bath. 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 nonconductive 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 at the selected point, C is the total current applied to the cell and L is the distance 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 vessel containing plating solution, into which vessel the cell will fit very closely, and improved electrolyte circulation and consequent improved temperature control is afforded, as more particularly described in an article appearing in "Plating," vol. 46, No. 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% 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 applying 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 1,500 milliliters (mls.) by subsequent addition of water. The bath is electrolyzed at a rate of about 20 to 30 amp-hours per gallon and is then ready for plating in the above-described modified Hull cell. In the Hull cell the graphite anodes are used and the cathode for each test is a 3¹⁵⁄16" by 2⅝" brass panel, each panel being nickel coated pror 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 7 specific current density levels as well as the total bright range. The chromium thickness reported at each density level is in micro-inches per 3-minute cycle. The current density range shown in the table is in amperes per square foot (ASF). The additive employed is dimethyl formamide and the concentrations employed as well as the temperature of operation are shown in the table below.

TABLE 1

Dimethyl formamide			Current density range (a.s.f.)[1]							Bright range (a.s.f.)
Ml.	Percent by vol.	Temp., ° F.	400	300	200	100	40	20	10	
0	0	80	3	4	7	12	13	10	5	500–6
25	1.67	82	4	5	9	10	10	8	5	900–5
50	3.34	80	19	15	9	9	8	6.5	4	1,000–5
50	3.34	94	22	16	15	13	10	6	4	1,000–6

[1] Chromium thickness reported in micro-inches per 3 min. cycle.

As shown in Table 1, without the addition of dimethyl formamide the bath exhibits a low rate of chromium deposition and a limited bright range coverage in the high current density areas. The addition of the organic additive greatly enhances this rate of chromium deposition and also results in an excellent extension of bright range coverage in the high current density area. Further, such extension and deposition is attained without severe deleterious affect on the plate deposition and range at the low current density region. As shown by the last two tests in the table, this extended bright range is maintained over a 14° F. difference in bath temperature with the elevated temperature resulting in an additional increase in the rate of deposition in the extreme high current density area.

EXAMPLE 2

A complex is formed in the manner of Example 1 and has a molar ratio of chromium to glycolic acid of 1:2.25 and a molar ratio of chromium to chloride of 1:0.625 and is added to water to provide a concentration of 0.78 gram mole of chromium per liter. To the bath there is also added 1 gram mole per liter of boric acid, 2 gram moles per liter of potassium chloride and the pH of the bath is adjusted, as shown in the table below, in the manner of Example 1. The final volume of the bath is adjusted to 1,500 milliliters by subsequent addition of water.

The bath is electrolyzed at a rate of about 20 to 30 amp-hours per gallon and thereafter a comparative plating test is run with no organic additive followed by plating tests using the organic additive bis-(2 - methoxy ethyl)-ether, as shown in the table below. Plating tests are carried out in the manner of Example 1 and results are reported in the table below in the manner of Example 1.

TABLE 2

Organic additive				Current density range (a.s.f.)								Bright range (A.S.F.)
Ml.	Percent by vol.	pH	Temp., ° F.	400	300	200	100	40	20	10	5	
0	0	2.96	102	10	14	18	25	20	10	4	N.R.	600–4
10	0.67	2.83	100	20	21	31	28	16	10	5	3	950–1
15	1.0	2.83	102	39	37	29	26	16	9	5	2.5	1,000–1
20	1.33	2.94	102	76	74	66	54	21	10	4.5	N.R.	1,000–3
20	1.33	2.8	98	62	59	48	40	17	8	3	N.R.	1,000–3
20	1.33	3.0	100	50	43	29	19	9	4	------	N.R.	1,000–7

NOTE.—N.R.=Not Recorded.

Without the organic additive, the above plating tests show that the bath provides a bright chromium range across the 600–4 a.s.f. range. Following the addition of the bis-(2-methoxyethyl)-ether, the bright range exhibits a highly desirable increase in the rate of deposition in the high current density area and extension of the bright range up to 1,000 ASF.

EXAMPLE 3

A complex is prepared in the manner of Example 1 and has a molar ratio of chromium to glycolic acid and of chromium to chloride as shown in Example 2. A plating bath is made up in the manner of Example 2 to contain a concentration of chromium, boric acid, potassium chloride as shown in Example 2. In the manner of Example 1 the pH of the bath is adjusted to 2.8 and the final volume of the bath is adjusted to 1,500 milliliters by the subsequent addition of water.

The bath is electrolyzed at a rate of about 20 to 30 amp-hours per gallon and a plating test is conducted without organic additive and then, in concentrations as shown in the table below, the organic additive diethylene glycol monomethyl ether is added to the bath. 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 3

Organic additive			Current density range (a.s.f.)							Bright range (a.s.f.)
Ml.	Percent by vol.	Temp., ° F.	400	300	200	100	40	20	10	
0	0	104	16	19	32	38	22	9	2.9	600–3
5	0.33	105	15	18	26	17	15	7	2.7	500–3
10	0.67	105	27	31	36	21	13	6	2.0	850–3
15	1.00	102	49	43	41	19	11	5	2.5	1,000–3
20	1.34	103	68	51	49	25	13	6	2.0	1,000–5

As shown in the table above a very minor amount of organic additive may lower the chromium rate of deposition and the upper limiting bright range, although such effect is not always observed. However, as further shown, as the concentration of such an additive is increased, the plating speed in the high current density area is desirably enhanced. Along with this, there is exhibited an excellent extension in the upper limit for the bright chromium range.

EXAMPLE 4

A plating bath is prepared by adding 42 weight parts of 50 percent chromium hydroxydichloride containing 50 weight percent of such compound dissolved in a balance of water, and 37 weight parts of 70 percent strength glycolic acid, into a reaction vessel followed by stirring of these substances in the vessel for 20 minutes. Thereafter, 32.5 weight parts of liquid potassium hydroxide containing 45 percent KOH in a balance of water, are slowly added to the reactor as agitation is continued. The reaction is exothermic and the temperature rises to above 165° F., as the addition is continued for 2 hours. Thereafter, 7.5 weight parts of water are added to the reactor and the mixture is permitted to cool.

There is then added sufficient potassium chloride to provide 125 grams per liter thereof, and sufficient boric acid to provide 56 grams per liter thereof. Water is then added to provide a total volume of 26.5 liters that contains sufficient complex to provide 40 g./l. of chromium, and the resulting material is stirred and heated to 120° F. while the pH is adjusted to 3.1 in the manner of Example 1.

The bath is then electrolyzed for a 20-hour period at 15 amperes and thereafter the pH is readjusted to 3.1 in the manner of Example 1. For plating tests, 1,500 milliliter portions of the resulting bath are taken and plating tests are carried out in a manner of Example 1 and results are reported in the table below. All plating tests are carried out at voltages of 12–14 volts and with bath temperatures at 72°–76° F.

TABLE 4

Bath additive		Plating speed at 400 a.s.f.[1]	Bright range, a.s.f.
Compound	Vol., mls.		
None	None	(2)	350–6
Tetrahydrofurfuryl alcohol	10	3	600–6
	10	3	600–6
	20	26	950–7
	30	38	950–7
1-(2-methoxypropoxy)-2-propanol	5	47	950–6
	10	(3)	950–10
Tetrahydrothiophene-1,1-dioxide	10	None	350–6
	20	None	375–6
	40	5	850–7
	50	14	925–6

[1] Chromium thickness reported in microinches per 3 min. cycle.

[2] Not measureable.

[3] Not recorded.

As shown by the results in the above table, addition of these additives provides an excellent enhancement in rate of chromium deposition, as well as in extension of bright range coverage, in the high current density area.

EXAMPLE 5

Into a reaction vessel containing 3,000 mls. water, there is added 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 taken and is blended with additives to provide the following amounts: 150 g./l. potassium chloride, 62 g./l. of H_3BO_3, and 86 mls. per liter glycolic acid of 70 percent strength. The pH of this bath is adjusted in the manner of Example 1 to a level as shown in the table below and the bath is electrolyzed for 20–30 amp-hours per gallon. Plating tests are then conducted with this bath and are carried out in a manner of Example 1 with the results being reported in the table below. All plating tests are carried out at voltages and at bath temperatures as shown in the table.

TABLE 5

Compound	Vol., mls./l.	Temp., ° F.	Volts	pH	Plating speed at 400 a.s.f.[1]
None	None	96	15	2.97	9
Bis(2-methoxyethyl) ether.	15.3	87	17.2	2.97	24
	23.3	94	15.7	3.07	30

[1] Chromium thickness reported in microinches per 3 min. cycle.

As is shown by the above results, the addition of the organic additive provides an excellent enhancement in the rate of chromium deposition for the bath containing the chromic glycolate complex.

What is claimed is:

1. An aqueous electrolytic plating bath for the plating of bright chromium plate and having enhanced electrodeposition of said plate, which bath comprises:

(A) a complex, water-soluble chromic compound for the deposition of chromium plate and containing non-aromatic carboxylic acid constituent containing less than about 10 carbon atoms and selected from the group consisting of dicarboxylic acids, monocarboxylic acids, monocarboxylic and dicarboxylic acids containing at least one hydroxyl group and mixtures thereof; and

(B) an organic component supplying substance in an amount not substantially above about 5 volume percent of said bath, which component is composed of at least one compound from group (1) or group (2) which are:

(1) polar aprotic substances having ready water dispersibility and selected from the group consisting of tetrahydrothiophene-1, 1-dioxide, dimethylsulfoxide, dimethylsulfone, dimethyl formamide, N-methylpyrrolidone, and mixtures thereof, and ring substituted derivatives of said substances that are cyclic polar aprotic substances, said derivatives having ring substituents other than hydrogen that are the same or different and are selected from the group consisting of hydroxyl, lower alkyl, lower alkoxy, hydroxyalkyl and dialkylamino, with there being less than four ring carbon atoms having said substituents; and

(2) cyclic and acyclic ethers and thioethers having an atomic ratio of oxygen atoms, or sulfur atoms, or both, to carbon atoms of greater than 0.25:1 and below 0.9:1.

2. The bath of claim 1 characterized by having a molar concentration of chromium of at least about 0.1.

3. The bath of claim 1 wherein said organic compounds of the group (2) are hydroxyl-containing compounds having not more than 3 hydroxyl groups and having molar ratio of OH:X, wherein X represents atoms selected from the group consisting of oxygen, sulfur, and their mixtures, of not above 3:1.

4. The bath of claim 1 wherein said organic component compounds of the group (2) are selected from the group consisting of bis(2-methoxy ethyl)ether, dipropylene glycol, tetraethylene glycol, butoxytriglycol, diethylene glycol monomethyl ether, 1-(2-methoxypropoxy)-2-propanol, tetrahydrofuran, tetrahydrofurfuryl alcohol, vinyl sulfide, and mixtures thereof.

5. The bath of claim 1 wherein said organic compounds of the group (2) are carboxyl-containing compounds having not more than two carboxyl groups and in a molar ratio of COOH:X, wherein X represents atoms selected from the group consisting of oxygen, sulfur, and their mixtures, of not above 1:1.

6. The bath of claim 1 wherein said bath is maintained within a pH of between about 1.8–4.9 and at a temperature not substantially above about 90° C.

7. The bath of claim 1 wherein said bath additionally contains 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.

8. The bath of claim 7 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 selected from the group consisting of perchlorate, chloride, and mixtures thereof and said bath contains between about 50–200 grams per liter of said salts.

9. The bath of claim 7 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 bath con-

tains between about 10–70 grams per liter of said substance.

10. A composition for maintaining an electrolytic plating bath for the plating of bright chromium plate as well as enhancing the electrodeposition of chromium plate from said bath, which composition comprises a blend of:

(A) a water soluble chromic plating compound containing non-aromatic carboxylic acid constituent containing less than about 10 carbon atoms and selected from the group consisting of dicarboxylic acids, monocarboxylic acids, monocarboxylic and dicarboxylic acids containing at least one hydroxyl group and mixtures thereof; and

(B) an organic component supplying substance in an amount not substantially above about 5 volume percent of said bath, which component is composed of at least one compound from group (1) or group (2) which are:

(1) polar aprotic substances having ready water dispersibility and selected from the group consisting of tetrahydrothiophene-1,1-dioxide, dimethylsulfoxide, dimethylsulfone, dimethyl formamide, N-methylpyrrolidone, and mixtures thereof, and ring substituted derivatives of said substances that are cyclic polar aprotic substances, said derivatives having ring substituents other than hydrogen that are the same or different and are selected from the group consisting of hydroxyl, lower alkyl, lower alkoxy, hydroxyalkyl and dialkylamino, with there being less than four ring carbon atoms having said substituents; and

(2) cyclic and acyclic ethers and thioethers having an atomic ratio of oxygen atoms, or sulfur atoms, or both, to carbon atoms of greater than 0.25:1 and below 0.9:1.

11. The method of enhancing the electrodeposition of bright chromium plate from an aqueous chromium plating bath containing a complex, water-soluble chromic plating compound, containing non-aromatic carboxylic acid constituent containing less than about 10 carbon atoms and selected from the group consisting of dicarboxylic acids, monocarboxylic acids, monocarboxylic and dicarboxylic acids containing at least one hydroxyl group, and mixtures thereof, which method comprises admixing with said bath an organic component in an amount supplying not substantially above about 5 weight percent of said component, basis weight of said bath, wherein said component is composed of at least one component from group (1) or group (2) which are:

(1) polar aprotic substances having ready water dispersibility and selected from the group consisting of tetrahydrothiophene-1,1-dioxide, dimethylsulfoxide, dimethylsulfone, dimethyl formamide, N-methylpyrrolidone, and mixtures thereof, and ring substituted derivatives of said substances that are cyclic polar aprotic substances, said derivatives having ring substituents other than hydrogen that are the same or different and are selected from the group consisting of hydroxyl, lower alkyl, lower alkoxy, hydroxyalkyl and dialkylamino, with there being less than four ring carbon atoms having said substituents; and

(2) cyclic and acyclic ethers and thioethers having an atomic ratio of oxygen atoms, or sulfur atoms, or both, to carbon atoms of greater than 0.25:1 and below 0.9:1.

12. The method of claim **11** wherein said bath is electrolyzed after said admixing and said bath contains after said admixing not substantially above about 5 volume percent, basis total volume of said bath, of said organic component.

13. The method of plating an article with bright chromium plate comprising passing a current between an anode and an article forming a cathode which are in contact with an aqueous chromium plating medium comprising:

(A) a complex, water-soluble chromic compound for the deposition of chromium plate and containing non-aromatic carboxylic acid constituent containing less than about 10 carbon atoms and selected from the group consisting of dicarboxylic acids, monocarboxylic acids, monocarboxylic and dicarboxylic acids containing at least one hydroxyl group and mixtures thereof; and

(B) an organic component supplying substance in an amount not substantially above about 5 volume percent of said bath, which component is composed of at least one compound from group (1) or group (2) which are:

(1) polar aprotic substances having ready water dispersibility and selected from the group consisting of tetrahydrothiophene-1,1-dioxide, dimethylsulfoxide, dimethylsulfone, dimethyl formamide, N-methylpyrrolidone, and mixtures thereof, and ring substituted derivatives of said substances that are cyclic polar aprotic substances, said derivatives having ring substituents other than hydrogen that are the same or different and are selected from the group consisting of hydroxyl, lower alkyl, lower alkoxy, hydroxyalkyl and dialkylamino, with there being less than four ring carbon atoms having said substituents; and

(2) cyclic and acyclic ethers and thioethers having an atomic ratio of oxygen atoms, or sulfur atoms, or both, to carbon atoms of greater than 0.25:1 and below 0.9:1.

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