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CHROMIUM PLATING BATH FOR ROTARY RECEPTACLE PLATING

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ABSTRACT OF THE DISCLOSURE

Desirable electrodeposition of bright chromium plate can be made on a substrate contained in a rotary receptacle immersed in a chromic plating medium. The medium contains a complex, water-soluble chromic compound for plating, which compound contains carboxylic acid constituents and halogen constituents. The plate obtained on the substrate within the rotary receptacle shows desirable, uniform chromium coverage over an extensive bright range.

BACKGROUND OF THE INVENTION

Decorative chromium plating from baths containing chromium in the trivalent state an association with at least carboxylic acid constituents has offered promise for commercial use; U.S. Pat. 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 using such baths for depositing chromium on substrates contained in a rotary receptacle such as barrel plating apparatus that is immersed in the plating medium, desirably uniform coverage may not always be obtained. Further the bright range achieved can be of limited coverage thereby detracting from the commercial potential of such bath for this type of plating.

SUMMARY OF THE INVENTION

It has now been found that bright chromium plate can be deposited on a substrate contained in a rotary receptacle immersed in a chromic plating medium. The medium for such plating contains a complex, water-soluble, chromic compound for the deposition of chromium plate, with this compound containing carboxylic acid constituents and halogen constituents. The plating achieved during the rotary recetpacle plating shows a very highly desirable and extended bright range. Moreover the chromium coverage achieved shows excellent uniformity and throwing power.

Broadly then, the invention is directed to the electrodeposition of bright chromium plate onto a substrate contained in a rotary receptacle immersed in a chromium plating medium, while the medium is supplied with a complex, water-soluble chromic compound for the deposition of chromium plate. This compound contains carboxylic acid constituents and halogen constituents selected from the group consisting of chlorine, fluorine, bromine, iodine and mixture thereof, with the complex having a molar concentration of chromium within the range from about 0.5 to about 1.5.

The invention is further directed to the method of chromium plating an article with a decorative chromium plate and onto such an article contained in a rotary receptacle immersed in a chromic plating medium, and further relates to the electroplated article thereby obtained.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electroplating medium contains some to all of 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 commercial plating operation, bromine and iodine are often not used, for economy and to avoid evolution of visible noxious fumes at the anode. Therefore chlorine and fluorine are almost exclusively used.

Although the water-soluble chromic compound need not have acid constituents representative of only an especial group of carboxylic acids, such acids which can or have been used for the chromic compounds are typically exemplified by monocarboxylic and dicarboxylic acids, with or without hydroxyl groups. For plating efficiency and water-solubility, advantageously the acids are non-aromatic acids containing less than about 10 carbon atoms and most preferably for efficiency have less than six carbon atoms and are unsaturated acids free from carbon-to-carbon unsaturation. Representative acids include glycolic acid, formic acid, oxalic acid and their mixtures. The compound of any of these acids such as a salt or ester thereof, which acts in any of the reactions such as those disclosed in more detail hereinbelow whereby the complex is formed, in the same manner as the free acid, can be used.

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 also thus advisable. Although these methods are not meant to be exhaustive concerning complex preparation, 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, which chromic halide is reacted with the carboxylic acid, 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 75 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 1.5. The complex is virtually always present in a bath wherein the liquid medium is supplied simply by water, plus a minor contribution from additional substances in liquid form. These additional substances can include excess acid used in the preparation of the complex.

However, typically for enhancing the chromium rate of deposition from the bath in the high current density area, minor amounts of organic additives can be added. These may be, added in liquid form, thereby contributing to the liquid medium of the bath. Such additives include polar aprotic substances which can be cyclic or acyclic organic materials or their mixtures. Representative of these additives are dimethyl formamide, tetrahydrofuran, dimethylsulfoxide, and mixtures thereof. Although some to all of these may form more than a very minor portion of the liquid medium, water, for economy, will supply the preponderant amount of such medium. These organic additives for enhancing the chromium rate of deposition in the high current density area may also be various ether, thioethers, glycol hydroxy ethers, such compounds that also contain carboxyl groups, and their mixtures. These ethers and other substances should have more than 4 carbon atoms within the range of 0.25:1 to 0.9:1.

The bath may also contain a sulfite component, for enhancing the chromium rate of deposition in the low current density area typically after considerable working of the bath, which component can be contributed by at least one compound, where such exists, of a metal sulfite, or metal bisulfite or metal meta bisulfite, or trialkylammonium bisulfite as well with mixtures of these. The substances may be added to the bath or formed in situ and those that are particularly preferred are the alkali metal and alkaline earth metal sulfites and bisulfites, e.g., sodium bisulfite.

The bath can further contain a salt of a strong acid preferably, for economy, an alkali metal salt; these 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 halide anions, from an acid having a dissociation constant of at least $K=10^{-2}$, for example chloride. The plating medium usually contains between about 50–200 grams per liter of such salts, basis liters of water in the plating medium. Such medium can also contain boric acid, or an equivalent to boric acid in aqueous solution, such as borax, boron oxide, or sodium oxyfluoborate. Such compounds may operate in the plating medium to augment the rate of deposition of the chromium and are typically used in amounts between about 10–70 grams per liter of the medium, basis liters of water in the medium.

Before deposition of chromium, the bath pH is adjusted to within a range depending upon the complex present, but typically is adjusted to a pH within the range from about 1.8 to 4.9. However, for example, a complex containing a substantial amount of fluorine as the halogen is 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, but is generally maintained during plating at a temperature within the range from room temperature, i.e., about 20° C. up to about 50° C. For those baths where the major amount of the complex contains fluorine, the temperature is usually maintained at a slightly more elevated temperature than for baths wherein chlorine provides the major amount of halide in the complex.

During plating, the object to be plated is made the cathode in the rotary receptacle and then 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 including bronze, nickel and copper-nickel plated zinc die castings. Additionally such plating can be performed on plastic surfaces which are activated or prepared for an electroplating operation, and the metallic surfaces to be plated are preferably activated prior to plating for production of a bright chromium plated finish.

The plating can be carried out in any rotary receptacle including those which may be more typically employed for plating copper, nickel or zinc, e.g., a barrel equipped with danglers acting as cathodes and that are most generally immersed in a plating bath and rotated therein during plating. Other serviceable cathode contacts include button type, chain danglers and metal barrel contact. Typically, such receptacles are rotated at a slow rate of about one revolution in two minutes to about twenty revolutions per minute. Also, intermittent action may be used, e.g., two minutes turning and 0.5 minute at rest. In any method, the contents of the receptacle to be plated are moved and turned by a cascading action.

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 to determine the bright plating range of the bath to be used for the barrel plating. The standard Hull cell is a trapezoidal box of non-conductive material and at the opposite ends of which are positioned anode and cathode plates, and as has been more particularly described in U.S. Pat. 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 also improved electrolyte circulation and consequent improved temperature control is afforded, as more particularly described in an article appearing in "Plating," volume 46, No. 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 percent strength, that is, 70 weight percent of glycolic acid in 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 increase this supplying heat to the reaction. As the reaction continues the temperature of the reaction medium reaches 71° C. without external heating and the chromium can be seen by visual observations 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 of the chro-

mium has dissolved. 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 solution is cooled and has a molar ratio of chromium atoms to glycolic acid of 1:2.25 and of chromium to chloride of 1:0.625. Sufficient of this resulting solution is then charged to a mixing tank, to provide 40 g./l. of chromium. There is then added 150 g./l. of potassium chloride, 63 g./l. boric acid and 10 milliliters per liter of bis-(2-methoxyethyl)ether. The pH of the bath is then adjusted to 3.1 by the addition of a sodium hydroxide solution in water. Additional water is used to bring the volume of the bath to 1000 milliliters. This bath is then electrolyzed at a rate of about 10 to 20 amp hours per gallon and is thereby prepared for use with a rotary receptacle for plating tests.

The rotary receptacle employed for the plating tests is a small barrel having a hexagonal cross section. The barrel is made by placing together, on adjacent long edges, six 6" x 2.5" panels, with each end being closed by an intimately fitting end panel. The barrel is typically employed for testing plating of copper, nickel and zinc, and has a 500 gram maximum load rating while operating at a rate of 1 revolution per 1.5 minutes. The barrel is equipped with two danglers that serve as cathodes and the barrel in use is immersed in a tank equipped with graphite anodes spaced approximately 8" from the barrel, one anode bar being placed alongside each long side of the barrel. Each of the six panels used in forming the barrel are equipped with a horizontal ⅛" key stock lifter installed inside and across each panel.

For plating tests in this barrel, there is used a load of 500 grams 0.25" x 20 round head, slotted, nickel-plated-brass, pre-buffed bolts which are first soaked in mineral spirits for initial cleaning and thereafter are rinsed and loaded in the barrel. The barrel ready for plating is then placed in a hot alkaline cathodic electro cleaning solution and the barrel rotated, and a current is then passed between steel anodes in the cleaner and the cathode danglers and load in the barrel at an intensity of 6 volts for a time of 3 to 5 minutes. Thereafter the barrel is removed from the cleaner, thoroughly rinsed, and is then immersed into an activating bath containing a strong acid, HCl or H_2SO_4 in a concentration of 5 percent by volume, for one minute, and subsequently removed and thoroughly rinsed.

The loaded barrel is then placed in the above-described bath and the circuit completed. Rotating of the barrel causes the bolts to move and cascade. A current of 30 amps and 7.0 volts is passed for 8 minutes and the bath is maintained at a temperature of 70° F. Thereafter the circuit for the barrel is disconnected, the barrel is removed from the bath and rinsed. The bolts are then manually removed from the barrel and are visually inspected and found to show highly desirable chromium plating coverage. The bath is thereby regarded to offer an excellent chromium plating medium for a rotary receptacle operation.

For comparison, a trivalent chromium plating bath is prepared as described in U.S. Pat. 3,006,823. The comparative system was prepared to contain the chromium glycolate complex described in the patent that, however, does not show a broad high performance coverage range of chromium plate and is not contemplated for use in the present invention. This comparative bath is made up to contain 150 g./l. potassium chloride and 72 g./l. boric acid in water and has a pH of about 3 as adjusted by sodium hydroxide. This comparative chromium glycolate complex from the U.S. Pat. 3,006,823 is the source for 52.1 g./l. of chromium in the bath and there is also present in the bath 86 milliliters per liter of glycolic acid of 70% strength. For plating tests in this comparative bath, 200 grams of 0.25 x 20" round head slotted, brass, pre-buffed bolts and 100 grams of steel bolts are prepared for plating. The preparation includes nickel plating and acid rinsing, followed by a final water rinsing.

In the manner described above, this load is plated in the barrel, except that the anodes are brought closer together to enhance plating, and the plating is conducted at about 35 amps and about 12.5–13 volts, for a time of 15 minutes. Upon visual inspection after plating and rinsing the bolts are seen to have a dull finish of incomplete covering not deemed to be acceptable.

The bright range for this comparative trivalent chromium plating solution prepared as described in U.S. Pat. 3,006,823 is a deposit from about 500 amps per square foot (a.s.f.) down to about 18 a.s.f. as measured on a modified Hull cell plating test carried out at 10 amps for 3 minutes at 82° F. This limited coverage in the extreme low current density area is inadequate to give good chromium plate covering in the barrel plating test, whereas the trivalent chromium plating bath used in the method of the present invention displays highly acceptable chromium coverage and uniformly of plate in the barrel plating test. Further, this plating bath used in the present invention achieves a bright range from 950 a.s.f. down to 3 a.s.f. on a comparable modified Hull cell plating test carried out at 10 amps and for 3 minutes.

Example 2

The barrel used in Example 1 is again used, but for determining the percent of acceptable articles that can be quickly and easily plated where many pieces per article, as well as several different articles are all present during the plating test. No comparative bath is used, but just a plating bath as first described in Example 1 containing a chromium plating complex from glycolic acid and with chlorine as the halogen constituent. The bath likewise contains 150 g./l. of potassium chloride and about 63 g./l. boric acid as well as the other constituents as shown in Example 1 including the pH adjustment such as shown in Example 1.

The barrel is prepared for plating as described in Example 1 and the articles for plating, which are shown in the table below are prepared for plating as shown in Example 1, such preparation including nickel plating and acid rinsing, followed by a final water rinsing. The total load for each plating test is 500 grams and the number of pieces of each article per test as well as the plating conditions of the test have been shown in the table below. After each test, the barrel is removed from the bath and rinsed, the articles in the barrel are then manually removed from the barrel and are visually inspected. The results of such testing and inspection are as follows:

TABLE

	Plating conditions			Bent hook screw		1.5-inch screw		0.5-inch screw	
Test	Amps	Time in minutes	Volts	No.	Percent O.K.	No.	Percent O.K.	No.	Percent O.K.
1	30	8	7.0	18	72.2	45	80	29	89.7
2	50	8	9.6	14	78.5	54	87.1	32	90.6

The above results, based not only on the total number of articles per test and the variety of the articles used, but also on the percent of acceptably plated articles in each test, demonstrate that the trivalent chromium plating bath used in the method of the present invention achieves very highly desirable chromium coverage and uniformity of plate in rotary receptacle plating operation.

I claim:

1. In the method of electrodepositing bright chromium plate onto a substrate contained in a rotary receptacle

immersed in the chromium plating medium, the improvement which comprises supplying said medium with a compound for the deposition of chromium plate that is 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, which compound contains carboxylic acid constituents supplied by acids selected from the group consisting of glycolic, oxalic, and mixtures thereof, said complex having a molar concentration of chromium within the range from about 0.5 to 1.5 and 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 method of claim 1 wherein said rotary receptacle is a barrel, said barrel is made a cathode for said electrodeposition, and said substrate is an activated plastic substrate.

3. The method 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 method of claim 1 wherein water supplies the preponderant amount of said medium, and said halogen is chlorine.

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