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**NOVEL CHROMIUM PLATING COMPOSITIONS
AND PROCESSES**

Fred Aoun, Madison Heights, Mich., assignor to
M & T Chemicals Inc., New York, N.Y.
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12 Claims

ABSTRACT OF THE DISCLOSURE

In accordance with certain of its aspects, this invention relates to novel compositions and to a process for electroplating chromium plate onto a basis metal which comprises passing current from an anode to a cathode at least a portion of which contains a conductive metal layer through an aqueous acidic chromium plating bath composition containing

- (1) At least one chromium compound providing hexavalent chromium ions for electroplating chromium; and
- (2) Bromate ion as cooperating additive to provide increased chromium throwing power; for a time sufficient to deposit a chromium electroplate having a thickness of at least 1×10^{-5} mm.

This invention relates to novel compositions and to novel processes for the electrodeposition of chromium from an aqueous acidic chromium plating bath.

It is known that chromium may be plated onto various basis metals from aqueous bath solutions. During chromium plating using such bath compositions it has been found that the use of certain catalysts such as silicofluoride ions and sulfate ions provide improved chromium electrodeposits especially in so-called low current density areas. The effect of such catalyst systems, however, has been found to vary with the concentration of the chromic acid and the ratio of the catalysts to the total chromic acid content. Since the concentration of the chromium plating bath continually varies during operation due to the removal of chromium in the form of deposited metal and due to the addition of impurities arising from the electrodes as well as decomposition products, it has been difficult to control and maintain the proper catalyst and chromic acid concentrations throughout the life of a typical aqueous acidic chromium electroplating bath.

It has now been found that the addition of bromate ions in combination with an aqueous acidic bath containing chromic acid results in a chromium electroplating composition which is stable over the life of the bath and provides a chromium electroplate of improved coverage. The bath compositions of the invention are further characterized by increased throwing power (i.e. the ability to provide satisfactory chromium electrodeposits in recessed areas and areas of non-uniform shape).

It is an object of this invention to provide improved electroplating compositions and processes. A further object of the invention is to provide chromium plating bath compositions which have good throwing power, excellent coverage, and extended useful life. Other objects of the invention will be apparent to those skilled in the art upon inspection of the following detailed description of the invention.

In accordance with certain of its aspects, this invention relates to novel compositions and to a process for electroplating chromium plate onto a basis metal which comprises passing current from an anode to a cathode at least a portion of which contains a conductive metal layer through an aqueous acidic chromium plating bath composition containing:

(1) At least one chromium compound providing hexavalent chromium ions for electroplating chromium; and

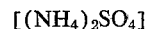
- (2) Bromate ion as cooperating additive to provide increased chromium throwing power; for a time sufficient to deposit a chromium electroplate having a thickness of at least 1×10^{-5} mm.

The chromium electroplating bath compositions of the invention may contain about 50-600 g./l. of chromic acid expressed as CrO_3 (preferably about 200-300 g./l. of chromic acid) and may be prepared from commercial chromic acid solutions. Preferably, a portion of the chromic acid used in the bath composition may be furnished by a salt of hexavalent chromium such as sodium chromate, sodium dichromate, potassium chromate, potassium dichromate, strontium chromate, magnesium dichromate, lanthanum chromate, lanthanum dichromate, etc. In many cases it may be advantageous to employ one or more of such salts in order to provide for a means of control of the composition or of the acidity of the aqueous chromium plating bath.

Catalyst anions may also be included in the aqueous chromium plating bath to regulate the concentrations of the active ingredients during electroplating. For example, sulfate, fluoride, and complex fluorides may be used. Typically, fluosilicates, fluoborates, fluoaluminates, fluotitanates, and fluozirconates may be included in the aqueous chromium plating bath composition without adversely affecting the properties of the novel chromium electroplate which is produced according to the invention. The fluoride ions may be added to the chromium electroplating bath in the form of compounds such as sodium silicofluoride (Na_2SiF_6), fluosilicic acid (H_2SiF_6), strontium silicofluoride (SrSiF_6), ammonium silicofluoride [$(\text{NH}_4)_2\text{SiF}_6$], magnesium silicofluoride (MgSiF_6), calcium silicofluoride (CaSiF_6) etc. Other fluoride compounds which may be used in the bath according to the invention include sodium fluoride, potassium fluoride, calcium fluoride, hydrofluoric acid, ceric fluoride, cerous fluoride, etc.

Other fluoride ions (including complex fluoride ions) which may be employed include, for example, fluoaluminates, fluoborates, fluotitanates, and fluozirconates.

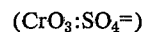
Sulfate ions may also be added to the chromium electroplating bath in the form of suitable sulfate compounds such as strontium sulfate (SrSO_4); sulfuric acid (H_2SO_4); lithium sulfate (Li_2SO_4); ammonium sulfate



calcium sulfate (CaSO_4); etc.

The total amount of combined catalysts may be present in the chromium plating bath composition in catalytic amounts (such as 0.01-5.0 g./l.) or in amounts of 0.01-100 g./l.

The chromium electroplating process may use temperatures of 30-70° C. with a chromic acid bath containing 100-600 g./l. of chromic acid (as CrO_3). When using sulfate, the ratio of chromic acid to sulfate ion

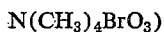


may be maintained at 100-550:1, typically 150-300:1 and preferably about 200:1.

Suitable neutralizers and/or buffers may also be employed in the bath composition of the invention. Examples of such neutralizers or buffers may include phosphates, borates, sulfonates, and carboxylates. In addition, catalyst anions as heretofore recited may also be used in amounts sufficient to act as buffers or neutralizers in combined effect with their catalyst properties.

Bromate ions may be added to the bath compositions of the invention in the form of salts such as alkali metal bromates (NaBrO_3 , KBrO_3 , LiBrO_3 , CsBrO_3); alkaline earth metal bromates [$\text{Ca}(\text{BrO}_3)_2$, $\text{Sr}(\text{BrO}_3)_2$ etc.]; ammonium bromate, (including alkyl-substituted ammonium

bromates such as tetramethylammonium bromate, etc.), chromium bromate, cerium bromate, aluminum bromate, magnesium bromate, etc. Any bath compatible source of bromate ion may be used (including organic bromates such as methyl bromate, etc.). Alkali metal and ammonium bromates (especially NH_4BrO_3 and



are preferred.

The bromate ion may be used in a chromium plating bath composition (containing about 100–600 g./l. of CrO_3) in effective amounts of about 0.01–10 g./l., preferably 0.05–5.0 g./l. of bromate (BrO_3^-) anion. Larger amounts of bromate ion may be used, but no additional improvement is obtained thereby and the use of excessive amounts of bromate ion serves to increase the cost factors of the novel chromium plating bath compositions and processes based thereon.

The basis material which may be treated according to this invention to produce an improved chromium deposit may include a basis material such as iron, steel, brass, bronze, copper, zinc, aluminum, magnesium, nickel, etc. either pure or in the form of an alloy or as multilayer deposits. The preferred basis metal to be plated in accordance with this invention may be steel, zinc, or brass which has first been plated with a conductive deposit such as a plate of bright nickel, typically preceded by a first plate of copper, bronze, or semi-bright nickel.

Other basis materials to be treated by the process of this invention may include plastics and resins including acrylonitrile-butadiene-styrene, acetals, acrylics, alkyls, alkyls, amines, cellulose, chlorinated polyethers, epoxies, furanes, fluorocarbons, isocyanates (urethanes), polyamides (nylons), phenoxides, phenolics, polycarbonates, polyesters, polyethylenes, silicones, polystyrenes, polyvinyls, and copolymers, etc. of these materials. When the basis material to be treated by the process of this invention is a plastic or resin, the surface thereof will be pre-treated by deposition thereon of a conductive deposit, such as a nickel deposit.

The basis material bearing a conductive surface, preferably a bright nickel plate, may be immediately treated after disposition of such plate or it may be water rinsed; or it may be rinsed, dipped in aqueous acid solution such as 0.5%–10%, say 2%, by weight of sulfuric acid prior to further treatment. The so-treated material may be dried or it may be further treated as is. If drying has been permitted, the conductive surface may be cleaned as by cathodically treating in alkaline cleaner followed by rinsing in water or dipping in an acid solution before further treatment.

According to this invention, the aqueous acidic chromium plating bath compositions which contain an effective amount of bromate ion may be employed at temperatures of about 30–70° C. to prepare improved chromium plated articles by passing current from an anode to a basis metal cathode through said aqueous acidic chromium plating solution at a temperature of 30–70° C. for a time sufficient to deposit a chromium electroplate having a thickness of at least 1×10^{-5} mm. Current densities which may be employed may be 1.0–90 amperes per square decimeter (a.s.d.) and preferably about 3–50 a.s.d. Especially good results may be obtained using pulsed or intermittent direct current. The bath compositions of the invention may be used with lead anodes and/or lead alloy anodes.

A typical bath composition which may be used in the invention to produce an improved chromium electrodeposit may comprise chromic acid in the amount of 50–600 g./l. as CrO_3 in combination with 0.01–10 g./l. of bromate ion. Other bath compatible materials may be incorporated in the bath. For example, inorganic sulfates and fluorides or complex fluorides and phosphates may be incorporated into the bath.

A specific bath composition may contain the following ingredients in the amounts indicated:

All amounts in grams
per liter (g./l.)

Chromic acid (CrO_3)	50–600
Sulfate ($\text{SO}_4^{=}$)	0.6–6
Bromate (BrO_3^-)	0.5–6
Acetic acid	10–25

The improved chromium deposit may be obtained using plating currents of 2–30 amperes per square decimeter (a.s.d.) at temperatures of 10°–80° C. using plating times of one-half minute to one hour (typically 2–30 minutes).

The following examples are submitted for the purpose of illustration only and are not to be construed as limiting the scope of the invention in any way.

EXAMPLE 1

An aqueous chromium plating bath composition containing the following ingredients in the indicated amounts (all amounts in grams per liter, g./l., unless otherwise specified) was prepared:

Ingredient:	Concentration (g./l.)
CrO_3	200
$\text{SO}_4^{=}$	3.5
$\text{SiF}_6^{=}$	2.0

A panel of buffed brass containing a 45° bend measuring 75 x 100 x 0.45 millimeters was cleaned and plated with a bright nickel deposit. The nickel plated panel was immersed in a Standard Hull Cell and the panel was connected as cathode. A total current of 8 amperes was passed through the solution for a time period of five minutes while maintaining the bath solution at about 35–45° C. The resulting chromium electrodeposit was satisfactory, but showed the usual minute defects in recessed areas of the bent portions of the test panel.

To the above solution was added 1.0–1.5 g./l. of bromate ion (added as potassium bromate salt) and an identical test panel was chromium plated in the Standard Hull Cell under the same conditions of temperature, plating current and time. The resulting chromium electrodeposit showed improved coverage and the bath composition provided improved throwing power.

Similar improved results are obtained using sodium bromate, ammonium bromate, strontium bromate etc. either with or without suitable catalysts such as sulfates, silicofluorides, etc.

EXAMPLE 2

The aqueous chromium plating bath composition of Example 1 was used with a mixture of 1.0 g./l. of NaBrO_3 and 1.0 g./l. of KBrO_3 . A buffed brass panel plated with a nickel strike was chromium plated using the time, temperature, and plating current of Example 1 to produce an excellent chromium plate over the bent surfaces of the test panel.

Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. A process for electroplating chromium plate onto a basis metal which comprises passing current from an anode to a cathode at least a portion of which contains a conductive metal layer through an aqueous acidic chromium plating bath composition containing:

- (1) at least one chromium compound providing hexavalent chromium for electroplating chromium, sulfate ions such that the ratio of chromic acid to sulfate ion is between 100:1 and 550:1; and
- (2) bromate ion as cooperating additive to provide increased chromium throwing power; for a time sufficient to deposit a chromium electroplate having a thickness of at least 1×10^{-5} mm.

2. A process as claimed in claim 1 wherein a portion of the bromate ion is provided by a bath compatible metal bromate or an ammonium bromate.

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3. A process as claimed in claim 1 wherein a portion of the bromate ion is provided by an alkali metal bromate or NH_4BrO_3 .

4. A process as claimed in claim 1 wherein a portion of the bromate ion is provided by at least one member selected from the group consisting of KBrO_3 , NaBrO_3 , and NH_4BrO_3 .

5. A process as claimed in claim 1 wherein the aqueous acidic chromium plating bath composition contains 50–600 g./l. of CrO_3 and 0.01–10 g./l. of bromate anion BrO_3^- .

6. A process as claimed in claim 1 wherein the aqueous acidic chromium plating bath composition contains:

(a) 50–600 g./l. of CrO_3 ;

(b) 0.01–100 g./l. of combined catalyst selected from the group consisting of sulfate ions and fluoride ions; and

(c) 0.01–10 g./l. of bromate anion BrO_3^- ; and wherein the aqueous acidic chromium plating bath composition is maintained at temperatures of 30–70° C.

7. A composition for electroplating chromium plate on a basis metal which comprises an aqueous acidic chromium plating bath composition containing:

(1) at least one chromium compound providing hexavalent chromium for electroplating chromium, sulfate ions such that the ratio of chromic acid to sulfate ion is between 100:1 and 550:1; and

(2) bromate as cooperating additive to provide increased chromium throwing power.

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8. A composition as claimed in claim 7 wherein a portion of the bromate ion is provided by a bath compatible metal bromate or an ammonium bromate.

9. A composition as claimed in claim 7 wherein a portion of the bromate ion is provided by an alkali metal bromate or NH_4BrO_3 .

10. A composition as claimed in claim 7 wherein a portion of the bromate ion is provided by at least one member selected from the group consisting of KBrO_3 , NaBrO_3 , and NH_4BrO_3 .

11. A composition as claimed in claim 7 wherein the aqueous acidic chromium plating bath composition contains 50–600 g./l. of CrO_3 and 0.01–10 g./l. of bromate anion BrO_3^- .

12. A composition as claimed in claim 7 wherein the aqueous acidic chromium plating bath composition contains:

(a) 50–600 g./l. of CrO_3 ;

(b) 0.01–100 g./l. of combined catalyst; and

(c) 0.01–10 g./l. of bromate anion BrO_3^- .

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