

1

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NOVEL CHROMIUM PLATING COMPOSITIONS
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14 Claims

ABSTRACT OF THE DISCLOSURE

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 solution containing:

- (1) at least one chromium compound providing hexavalent chromium ions for electroplating chromium; at least one catalyst selected from the group comprising sulfate ions and fluoride ions, and
- (2) at least one member of the group consisting of sulfoacetic acid, isethionate and isethionic acid; for a time sufficient to deposit a chromium electroplate having a thickness of at least 1×10^{-4} millimeter.

This invention relates to a novel process for the electro-deposition of chromium and to the novel chromium deposits formed thereby. This invention also relates to chromium surface layers on wearing parts and touching parts in relative motion, such as piston rings in cylinders, bearings, and turbine edges.

The hardness of chromium delays the proper seating, or formation of a tight joint. As a practical matter, it is not possible to machine all moving parts to tolerances which will provide an exact fit and, ordinarily, conformation of the parts is obtained during an initial period of actual operation which causes the parts to accommodate themselves to one another. This process of accommodation is generally referred to as "breaking-in."

An object of the present invention is to provide a chromium bearing surface which has quick "break-in" characteristics while retaining the excellent wearing qualities and long life of such surfaces.

Another object of this invention is to provide a process for electrodepositing bright decorative chromium plate.

Other objects of the invention will be apparent to those skilled in the art upon inspection of the following detailed description of the invention.

This invention relates to novel compositions and to a process for electroplating decorative 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 solution containing:

- (1) at least one chromium compound providing hexavalent chromium ions for electroplating chromium; at least one catalyst selected from the group comprising fluoride ions and sulfate ions, and
- (2) at least one member of the group consisting of sulfoacetic acid, isethionate and isethionic acid.

The chromium electroplating bath compositions of the invention contain about 100–600 grams per liter of chromic acid (expressed as CrO_3) and preferably about 100–200 grams per liter of chromic acid.

The plate produced by the novel process of this invention is highly satisfactory with respect to its unusually bright decorative appearance.

According to another of its aspects this invention is a

2

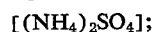
method of forming a bearing surface upon a substrate comprising a duplex plating of two disparate kinds of chromium comprising:

- (1) electrodepositing a hard chromium first layer and then
- (2) electrodepositing on said first layer of hard chromium a layer of microcrack chromium having at least 40 cracks per centimeter comprising maintaining an aqueous chromium plating bath containing chromic acid, sulfate ions, active fluoride ions, and at least one member of the group consisting of:
 - (a) sulfoacetic acid
 - (b) isethionate
 - (c) isethionic acid

According to another of its aspects this invention relates to a piston ring comprising an inner annular portion, an intermediate contiguous hard chromium portion, and an outer annular portion of microcracked chromium.

While sulfoacetic acid itself imparts homogeneous microcracking, isethionates, such as sodium isethionate, are readily oxidized to sulfoacetic acid by the chromic acid plating bath and also effect enhanced microcracking of chromium. Thus it has been found that sulfoacetic acid has been found to produce a very different structure in heavy chromium deposits. The amount of sulfoacetic acid added to the chromic acid bath should be between 1 gram per liter and 10 grams per liter, preferably about 3 grams per liter.

Sulfate ions may 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 chromium electroplating process uses temperatures of 30–70° C. with a chromic acid bath containing 100–600 grams per liter of chromic acid (as CrO_3). The ratio of chromic acid to sulfate ion ($\text{CrO}_3:\text{SO}_4^{2-}$) should be maintained at 50–550:1, typically 150–300:1 and preferably about 200:1.

The aqueous chromium plating bath contains active fluoride. Active fluoride is fluoride ion in the form exhibiting catalytic activity in the bath. Active fluoride may be in the form of simple fluoride, F^- , or complex fluoride. Where complex fluorides are employed, one mole of complex fluoride may be considered equivalent to one mole of simple fluoride ion, i.e. both contribute approximately one mole of active fluoride to the bath. Typically, the active fluoride may be selected from the group consisting of fluoride (F^-), and complex fluorides including fluosilicate or silicofluoride (SiF_6^{2-}), fluoborate (BF_4^-), fluoaluminate (AlF_6^{3-}), fluophosphate (PF_6^-), fluozirconate (ZrF_6^{2-}), and fluotitanate (TlF_6^-). Fluosilicate may be the most preferred active fluoride.

The active fluoride may typically be present in the aqueous chromium plating bath in the amount of about 0.0005–0.15 mole per liter. Preferably 0.01–0.05 mole per liter of active fluoride may be present. The active fluoride may be introduced into the bath by dissolving therein a salt or an acid of the active fluoride. Preferably, an alkali metal salt may be employed. Examples of suitable sources of active fluoride include sodium fluoride, potassium silicofluoride, fluoboric acid, sodium fluoaluminate, potassium fluophosphate, sodium bifluoride, potassium bifluoride, sodium fluotitanate, sodium fluozirconate, ammonium fluosilicate, and lithium fluosilicate.

Preferably, the aqueous chromium plating bath also contains sulfate ion, typically in the amount of about 0.2–5.0 grams per liter and preferably 0.3–4.0 gram per

liter, say 1-3 grams per liter. The presence of sulfate ion improves the microcrack effect and the appearance of the chromium deposit and lowers plating time. The sulfate ion may be provided by dissolving in the bath sulfuric acid or a salt thereof having sufficient solubility to produce the desired concentration. Suitable sources of sulfate ion include sulfuric acid, sodium sulfate, potassium sulfate, magnesium sulfate, strontium sulfate, calcium sulfate, etc. The bath may contain common ion salts, e.g. K^+ , Sr^{++} , Ca^{++} , La^{+++} , and other rare earth cations or mixtures thereof to limit the solubility of the catalyst ions to a desirable value in a self-regulating system.

The highly preferred aqueous chromium plating baths contain, in addition to chromic acid, sulfate, at least one member of the group consisting of sulfoacetic acid, isethionate and isethionic acid, active fluoride; selenium in soluble form. Soluble selenium may be introduced into the bath by dissolving therein a compound containing selenium which is soluble in the bath. Illustrative useful compounds include selenic acid and salts thereof, such as sodium selenate, ammonium selenate, potassium selenate, selenous acid and salts thereof, such as sodium selenite, potassium selenite; lower alkyl esters of selenic acid and selenous acid such as dimethyl selenate, diethyl selenate, di-n-propyl selenate, di-sec-butyl selenate, dimethyl selenite, diethyl selenite, di-isopropyl selenite, di-n-butyl selenite, etc. Other compounds capable of contributing selenium in soluble form may also be employed.

The most preferred form of soluble selenium is selenate. Typically, the selenium is present in the bath in the amount of 0.50×10^{-5} mole per liter Se and preferably 3×10^{-5} - 15×10^{-5} mole per liter Se. The baths containing selenium, preferably selenate, within the noted ranges produce an exceptionally dense, fine microcrack pattern on cathodes plated according to the process of this invention.

The most highly preferred aqueous chromium plating baths may contain chromic acid, active fluoride preferably fluosulfate, sulfate, and selenium, preferably selenate.

In accordance with certain embodiments of this invention, the aqueous chromium plating bath may contain:

Component	Typical	Preferred	Highly preferred
Chromic acid (g./l.)	100-500	150-400	150-400
Active fluoride (mole/l.)	0.005-0.15	0.01-0.15	0.01-0.05
Sulfate (g./l.)	0.2-5	0.3-4	1-3
Selenium (mole/l.)	0.50×10^{-5}	0.15×10^{-5}	3×10^{-5} - 15×10^{-5}

Cerous ions may be added to the bath in the form of salts such as cerium carbonate, cerium fluoride, cerium sulfate, etc. When cerium fluoride (CeF_3) is employed in combination with fluoride, fluoride-containing and/or sulfate catalysts, the chromium plating bath composition (containing 100-600 grams per liter of CrO_3) may be saturated with CeF_3 . Such saturation is provided to obtain self-regulation of the catalyst content of the bath. Typically, from about 1 gram per liter to 4 grams per liter or more of CeF_3 (or other cerous salts including complex fluoride salts) may be added to a chromium plating solution containing 100-600 grams per liter CrO_3 to form a chromic acid solution which contains an excess of undissolved cerium fluoride (CeF_3).

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

A 550 milliliter Hull Cell was used with an ordinary bath containing 200 grams per liter of chromic acid and 2.0 grams per liter of sulfate and 3.0 grams per liter of sulfoacetic acid to plate brass Hull Cell panels which had been nickel plated at 10 amperes for 10 minutes. After nickel plating the panels were given a water rinse, acid dip (10% sulfuric acid) and another water rinse. The panels were then placed in a slotted Hull Cell in a polyvinyl chloride tank and plated at 8 amperes for 8 minutes. The effect of adding 3 grams per liter of sulfoacetic acid

to this ordinary bath was that of enhanced microcracking.

EXAMPLE 2

A 500 milliliter Hull Cell was used with an all soluble salt bath of the following composition:

	G./l.	Oz./gal.
Chromic acid (CrO_3)	175	23.4
Sulfate (SO_4)	0.875	0.117
Fluosilicate (SiF_6)	0.375	0.050

3 grams per liter of sulfoacetic acid were added to the bath to plate brass Hull Cell panels which had been nickel plated at 10 amperes for 10 minutes. After nickel plating the panels were given a water rinse, acid dip (10% sulfuric acid) and another water rinse. The panels were then placed in a slotted Hull Cell in a polyvinyl chloride tank and plated at 8 amperes for 8 minutes. The effect of adding 3 grams per liter of sulfoacetic acid to this ordinary bath was that of enhanced microcracking.

EXAMPLE 3

Hull Cell panels were also plated using the following chromium plating bath composition:

	G./l.	Oz./gal.
Chromic acid (CrO_3)	175	23.4
Sulfate (SO_4)	0.58	0.08
Sodium sulfate (Na_2SO_4)	0.86	0.11
Fluoride (F^-)	0.30	0.04
Cerous fluoride (CeF_3)	2.50	0.33

With the addition of 6 grams per liter of sulfoacetic acid using the same procedure as in Example 1, except that the plating time was 6 minutes, again enhanced microcracking was attained, substantiating that the microcracked chromium of this invention was useful for "break-in" and other lubricity-demanding applications.

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.

We 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 solution containing:

(1) 100 grams per liter to 600 grams per liter of at least one chromium compound providing hexavalent chromium ions for electroplating chromium; at least one catalyst selected from the group comprising 0.2 gram per liter to 5.0 grams per liter of sulfate ions and 0.0005 mole per liter to 0.15 mole per liter of fluoride ions; and

(2) 1 gram per liter to 10 grams per liter of at least one member of the group consisting of sulfoacetic acid, isethionate and isethionic acid; for a time sufficient to deposit a chromium electroplate having a thickness of at least 1×10^{-4} millimeter.

2. The process of claim 1 wherein said process is one for electrodepositing a bright decorative chromium plate and said isethionate is sodium isethionate.

3. A process for electroplating chromium plate onto a basis metal as claimed in claim 1 wherein the aqueous acidic chromium plating solution contains about 100-600 grams per liter of chromic acid.

4. A process for electroplating chromium plate onto a basis metal as claimed in claim 1 wherein the electroplating process is carried out at 30-70° C.

5. A process for electroplating chromium plate onto a basis metal as claimed in claim 1 wherein the aqueous acidic chromium plating solution contains about 100-600 grams per liter of chromic acid and is saturated with a cerous salt at 30-70° C.

6. A process for electroplating chromium plate onto a basis metal as claimed in claim 1 wherein the aqueous

5

acidic chromium plating solution contains about 100-600 grams per liter of chromic acid and about 3 grams per liter of at least one member of the group consisting of sulfoacetic acid, isethionate and isethionic acid.

7. A process for electroplating chromium plate onto a basis metal as claimed in claim 1 wherein the aqueous acidic chromium plating solution contains about 200-350 grams per liter of chromic acid and about 3 grams per liter of at least one member of the group consisting of sulfoacetic acid, isethionate and isethionic acid.

8. A process for electroplating chromium plate onto a basis metal as claimed in claim 1 wherein the aqueous acidic chromium plating solution contains about 200-400 grams per liter of chromic acid, about 1-4 grams per liter of cerous salt, and wherein the chromic acid to sulfate ion ratio is 100-550:1.

9. A composition for electroplating chromium plate onto a basis metal which comprises:

(1) 100 grams per liter to 600 grams per liter of at least one chromium compound providing hexavalent chromium ions in aqueous media for electroplating chromium, 0.2 grams per liter to 5.0 grams per liter of sulfate ions as catalysts; and

(2) 1 gram per liter to 10 grams per liter of at least one member of the group consisting of sulfoacetic acid, isethionate and isethionic acid.

10. A composition for electroplating chromium plate onto a basis metal as claimed in claim 6 wherein the concentration of chromic acid is about 100-600 grams per liter.

11. A composition for electroplating chromium plate onto a basis metal as claimed in claim 6 wherein the concentration of chromic acid is about 200-350 grams per liter and the composition for electroplating is saturated with a cerous salt at 30-70° C.

6

12. A composition for electroplating bright decorative chromium plate onto a basis metal as claimed in claim 6 wherein the concentration of chromic acid is about 200-350 grams per liter and the composition for electroplating contains about 3.0 grams per liter of at least one member of the group consisting of sulfoacetic acid, isethionate, and isethionic acid.

13. A composition for electroplating chromium plate onto a basis metal as claimed in claim 6 wherein the concentration of chromic acid is 200-350 grams per liter and the composition for electroplating contains 1-4 grams per liter of CeF_3 .

14. A composition for electroplating chromium plate onto a basis metal as claimed in claim 6 wherein the concentration of chromic acid is about 200-400 grams per liter, the chromic acid to sulfate ion ratio is 50-550:1, and the composition for electroplating contains about 3 grams per liter of at least one member of the group consisting of sulfoacetic acid, isethionate and isethionic acid.

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