Provided is hard trivalent chromium plating solution having improved covering power. The trivalent chromium plating solution comprises a trivalent chromium compound comprising a compound of formula (1) below:

\[ \text{Cr}_5\text{SO}_4\text{H}_6\text{OH}_{6+2n} \quad (0 < n) \]  

(1)
ADD TRIVALENT CHROMIUM COMPOUND TO HEATED, DISTILLED WATER AND STIR TRIVALENT CHROMIUM COMPOUND

FILTER SOLUTION HAVING TRIVALENT CHROMIUM COMPOUND DISSOLVED THEREIN

ADD BUFFER AGENT AND CONDUCTIVITY AGENT TO FILTERED SOLUTION AND DISSOLVE BUFFER AGENT AND CONDUCTIVITY AGENT

ADD COMPLEXING AGENT TO SOLUTION HAVING BUFFER AGENT AND CONDUCTIVITY AGENT

MAINTAIN SOLUTION HAVING COMPLEXING AGENT AT 70 TO 80°C FOR PREDETERMINED PERIOD OF TIME

COOL SOLUTION MAINTAINED AT 70 TO 80°C FOR PREDETERMINED PERIOD OF TIME

ADD PLATING ACTIVATING AGENT TO COOLED SOLUTION AND DISSOLVE PLATING ACTIVATING AGENT

MAINTAIN SOLUTION HAVING PLATING ACTIVATING AGENT DISSOLVED THEREIN AT 40 TO 50°C FOR PREDETERMINED PERIOD OF TIME

COOL SOLUTION MAINTAINED AT 40 TO 50°C FOR PREDETERMINED PERIOD OF TIME

ADJUST HYDROGEN ION INDEX OF SOLUTION BY ADDING HYDROGEN ION INDEX ADJUSTING AGENT, IF NECESSARY

ADD WETTING AGENT TO SOLUTION HAVING ADJUSTED HYDROGEN ION INDEX

ADJUST HYDROGEN ION INDEX OF SOLUTION AGAIN BY ADDING HYDROGEN ION INDEX ADJUSTING AGENT, IF NECESSARY

END
FIG. 2

START

PREPARE TRIVALENT CHROMIUM PLATING SOLUTION IN PLATING BATH  
(\textbf{S300})

IMMERSE OBJECT TO BE PLATED IN TRIVALENT CHROMIUM PLATING SOLUTION  
(\textbf{S310})

APPLY NEGATIVE POTENTIAL TO OBJECT TO BE PLATED  
AND APPLY POSITIVE POTENTIAL TO INSOLUBLE ANODE  
AFTER INSTALLING INSOLUBLE ANODE IN PLATING BATH  
(\textbf{S320})

END
TRIVALENT CHROMIUM PLATING SOLUTION AND PLATING METHOD USING THE SAME

RELATED APPLICATION

[0001] This application claims priority from Korean Patent Application No. 10-2010-0073495 filed on Jul. 29, 2010 in the Korean Intellectual Property Office, the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a trivalent chromium plating solution and a plating method using the same, and more particularly, to a hard trivalent chromium plating solution having improved covering power.

[0004] 2. Description of the Related Art

[0005] Chrome plating is the most common process among various plating processes and is a final treatment step. Chrome plating may be classified into decorative plating for obtaining a beautifully glossy metal surface and hard plating for increasing wear resistance.

[0006] In the case of decorative plating, the plating thickness typically ranges from 0.2 to 0.5 μm. Decorative plating is usually used to plate brass surfaces of tableware and other disposable products. In the case of hard plating, the plating thickness may range from approximately 5 to several tens of μm although it varies according to the required wear life. Hard plating is used to prevent a portion of a camera lens to which a screw is tightened, a precision machine, an inner surface of a mold, a surface of a printing plate, etc. from wearing out.

[0007] In hexavalent chromium plating, electroplating is typically performed using a solution of chromic acid (CrO₃) mixed with sulfuric acid (H₂SO₄). For an anode, an element that is not eroded by H₂SO₄, such as lead, is used instead of chromium metal. Electrodeposition is continuously performed while CrO₃ supplement a reduction of chromium in the solution.

[0008] The concentration of CrO₃ in a plating solution used for chrome plating may be high or low, and various forms of coatings can be obtained depending on the temperature of the solution and current density, that is, plating conditions. Advantages of hexavalent chromium plating include excellent reflectivity, color and corrosion resistance as well as high current efficiency.

[0009] Despite these advantages, hexavalent chromium plating produces CrO₃ gas that is fatal to the human body during the plating process. In particular, hexavalent chromium ions introduced into underground water or rivers may cause deadly environmental contamination. Therefore, hexavalent chromium must be reduced to trivalent chromium.

[0010] That is, hexavalent chromium is classified as a carcinogen by the International Agency of Research on Cancer (IARC). Since the use of hexavalent chromium is expected to be prohibited, alternatives to hexavalent chromium are required. Accordingly, a lot of research is being actively conducted worldwide to develop alternatives to hexavalent chromium.

[0011] Examples of alternatives to hexavalent chromium plating include ion-nitriding, plasma spraying, and ion plating. However, these alternatives require 5 to 10 times the cost of hexavalent chromium plating and cannot be applied to large-sized products.

SUMMARY OF THE INVENTION

[0012] For these reasons, chrome plating using trivalent chromium is being recognized as the most efficient alternative.

[0013] However, a conventional trivalent chromium plating solution does not have superior covering power. Thus, it is difficult to apply electrolyplating on surfaces of machine parts or products having complicated shapes.

[0014] Aspects of the present invention provide a trivalent chromium plating solution having superior covering power.

[0015] However, aspects of the present invention are not restricted to the one set forth herein. The above and other aspects of the present invention will become more apparent to one of ordinary skill in the art to which the present invention pertains by referencing the detailed description of the present invention given below. According to an aspect of the present invention, there is provided a trivalent chromium plating solution comprising a trivalent chromium compound including a compound of formula (1) below;

wherein Crₓ(SO₄)₃OHₖ₋ₓₜₐₓ (x<3) (1).

[0016] According to another aspect of the present invention, there is provided a plating method comprising preparing a trivalent chromium plating solution in a plating bath, immersing an object to be plated in the trivalent chromium plating solution, and applying a negative potential to the object to be plated and applying a positive potential to an insoluble anode after installing the insoluble anode in the plating bath, wherein the trivalent chromium plating solution comprises a trivalent chromium compound comprising a compound of formula (1) below, a complexing agent suppressing a polymerization reaction of the trivalent chromium compound in the plating solution, a conductivity agents increasing electrical conductivity of trivalent chromium ions, a buffer agent stabilizing a hydrogen ion index of the plating solution, a plating activating additive increasing adhesive power and capability of forming a plated layer, a wetting agent removing a pitting phenomenon which occurs on a plated surface, and a hydrogen ion index adjusting agent adjusting the hydrogen ion index of the plating solution,

wherein Crₓ(SO₄)₃OHₖ₋ₓₜₐₓ (x<3) (1).

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The above and other aspects and features of the present invention will become more apparent by describing in detail exemplary embodiments thereof with reference to the attached drawings, in which:

[0018] FIG. 1 is a process flowchart illustrating a method of preparing a trivalent chromium solution according to the present invention; and

[0019] FIG. 2 is a flowchart illustrating a plating process using a trivalent chromium plating solution according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0020] The present invention will now be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.
A trivalent chromium plating solution according to the present invention may include a trivalent chromium compound which provides trivalent chromium ions, a complexing agent which suppresses a polymerization reaction of the trivalent chromium compound in the plating solution, a conductivity agent which increases electrical conductivity of the trivalent chromium ions, a buffer agent which stabilizes a hydrogen ion index of the plating solution, a plating activating agent which increases adhesive power and capability of forming a plated layer, a wetting agent which removes a pitting phenomenon that occurs on a plated surface, and a hydrogen ion index adjusting agent which adjusts the hydrogen ion index of the plating solution.

The trivalent chromium compound includes a compound of formula (1) below.

\[ \text{C}_\text{3} \text{(SO}_4\text{)}_\text{n} \text{OH}_{\text{2} \times \text{n}} \text{ (n<3) } \]  

(1).

The trivalent chromium compound may be added to the trivalent chromium plating solution in an amount of 0.4 mol/L to 1.3 mol/L, particularly, 0.8 mol/L to 1 mol/L. Trivalent chromium contained in the trivalent chromium compound forms a chromium film.

The complexing agent may prevent the trivalent chromium ions contained in the trivalent chromium compound from being polymerized in the plating solution. The complexing agent may be, for example, formic acid, alkali metal formate, or ammonium formate, but is not limited thereto. The complexing agent may be added to the trivalent chromium plating agent in an amount of 0.05 to 2 mol/L, particularly, 0.4 to 0.6 mol/L.

The conductivity agent may facilitate the formation of a chromium film by increasing electrical conductivity when an object to be plated is immersed in the trivalent chromium plating solution so as to be plated. The conductivity agent may be, for example, sodium sulfate, but is not limited thereto. The conductivity agent may be added to the trivalent chromium plating solution in an amount of 0.1 mol/L to 0.8 mol/L, particularly, 0.2 mol/L to 0.4 mol/L.

The buffer agent enables the hydrogen ion index (pH) of the trivalent chromium plating solution to remain stably within a predetermined range. The buffer agent includes boric acid and aluminum sulfate. As the buffer agent, when both boric acid and aluminum sulfate exist, the trivalent chromium plating solution, high-quality plating can be obtained. Boric acid may be contained in the trivalent chromium plating solution in an amount of 0.08 to 1 mol/L, particularly, 0.4 to 0.6 mol/L. Aluminum sulfate may be contained in the trivalent chromium plating solution in an amount of 0.05 to 0.2 mol/L, particularly, 0.1 to 0.16 mol/L.

The plating activating agent facilitates plating using low-current, thereby expanding an effective plating current range. The plating activating additive may be, for example, carbamide, but is not limited thereto. The plating activating agent may be contained in the trivalent chromium plating solution in an amount of 0.1 to 1.2 mol/L, particularly, 0.4 to 0.6 mol/L.

The wetting agent may remove the pitting phenomenon that occurs on a plated surface. The wetting agent may be a surfactant. An example of the surfactant is an organic anion-active surfactant containing a sulfonate group, but is not limited thereto. An example of the organic anion-active surfactant is sodium lauryl sulfate (C\text{12}H\text{25}SO\text{Na})

The wetting agent may be contained in the trivalent chromium plating solution in an amount of 0.01 to 1 g/L, particularly, 0.05 to 0.1 g/L.

The hydrogen ion index adjusting agent may adjust the hydrogen ion index of the trivalent chromium plating solution. The hydrogen ion index adjusting agent may be, for example, sulfuric acid (H\text{2}SO\text{4}), sodium hydroxide (NaOH), or sodium carbonate (Na\text{2}CO\text{3}), but is not limited thereto. The hydrogen ion index adjusting agent may be added to the trivalent chromium plating solution in an amount that allows the hydrogen ion index of the trivalent chromium plating solution to be in a range of, e.g., 1.1 to 3.5, particularly, 1.4 to 1.8.

Hereinafter, a method of preparing a trivalent chromium plating solution according to the present invention will be described with reference to FIG. 1. FIG. 1 is a process flowchart illustrating a method of preparing a trivalent chromium solution according to the present invention.

Referring to FIG. 1, a trivalent chromium compound is added to heated, distilled water and is then stirred (operation S100). Here, the temperature of the distilled water may be approximately 70 to 95°C, and the trivalent chromium compound is stirred until it is completely dissolved in the distilled water.

The solution having the trivalent chromium compound dissolved therein is filtered (operation S110). The solution may be filtered using a paper filter, a fiber filter, or other types of filters.

A buffer agent and a conductivity agent are added and dissolved in the filtered solution (operation S120). Here, the temperature of the solution may be 70 to 80°C, and the added buffer agent and conductivity agent may be solid. The above solid elements should be completely dissolved in the solution.

Next, a complexing agent is added to the solution in which the buffer agent and the conductivity agent have been dissolved (operation S130). The solution having the buffer agent and the conductivity agent dissolved therein is maintained at a temperature of 70 to 80°C, and the complexing agent is slowly added to the solution.

A plating bath is covered with a covering member, and the solution having the complexing agent added thereto is maintained at 70 to 80°C for a predetermined period of time, for example, for approximately one hour (operation S140).

Next, the solution maintained at 70 to 80°C for the predetermined period of time is cooled (operation S150). The solution may be cooled to approximately 40 to 50°C.

A plating activating agent is added and dissolved in the cooled solution (operation S160). The plating activating agent may be solid and is completely dissolved in the solution at a temperature of 40 to 50°C.

Then, the plating bath is covered with the covering member, and the solution having the plating activating agent dissolved therein is maintained at a temperature of 40 to 50°C for a predetermined period of time, for example, for approximately one hour (operation S170).

The solution maintained at 40 to 50°C for the predetermined period of time is cooled (operation S180). The solution may be cooled to room temperature.

The volume of a plating solution is adjusted by adding distilled water to the cooled solution. In addition, a hydrogen ion index of the solution is measured, and, if necessary, the hydrogen ion index of the solution is adjusted by adding a hydrogen ion index adjusting agent to the solution (operation S190).

Next, a wetting agent is added to the solution having the adjusted hydrogen ion index (operation S200). Specifically, the wetting agent may be added in a predetermined concentration to distilled water, and the distilled water having the wetting agent may be added to the solution having the adjusted hydrogen ion index.
Distilled water is added to the solution having the wetting agent in order to reach the final volume of the plating solution. Then, the hydrogen ion index of the solution is measured, and, if necessary, the hydrogen ion index of the solution is adjusted again by adding the hydrogen ion index adjusting agent (operation S210).

Hereinafter, a plating process using a trivalent chromium solution according to the present invention will be described with reference to FIG. 2. FIG. 2 is a flowchart illustrating a plating process using a trivalent chromium plating solution according to the present invention.

Referring to FIG. 2, a trivalent chromium plating solution according to the present invention is prepared within a plating bath (operation S300). Then, an object to be plated is immersed in the trivalent chromium plating solution (operation S310).

A negative potential is applied to the object to be plated. In addition, an insoluble anode is installed in the plating bath, and a positive potential is applied to the insoluble anode (operation S320). Here, the insoluble anode may be, for example, a titanium-manganese dioxide anode (TMDA), a dimensionally stable anode (DSA) having iridium oxide (IrO₂) or ruthenium oxide (RuO₂) formed on a porous titanium plate, or a platinumized titanium anode, but is not limited thereto. In particular, TMDA does not require spatial separation of a cathode and an anode in a plating process and does not release toxic chlorine gas during the plating process. Furthermore, TMDA noticeably reduces an electrochemical oxidation reaction from trivalent chromium to hexavalent chromium.

When power is supplied, the current density may be 15 to 30 A/dm², particularly, 10 to 20 A/dm².

During the plating process, a hydrogen ion index of the plating solution may be maintained at 1.1 to 3.5, particularly, 1.4 to 1.8. In addition, the plating bath may be maintained at a temperature of 20 to 60°C, particularly, 30 to 40°C.

A chromium-plated film may have a thickness of several tens of μm.

Hereinafter, the present invention will be described in greater detail by way of specific embodiments and a comparative example.

**Embodiment 1**

To prepare 1 L of plating solution, 1 mol of the compound of formula (1) was added to 0.5 to 0.7 L of heated, distilled water and was stirred at 70 to 95°C until it was completely dissolved.

\[
C_{12}(SO_4)_2(OH)_{26}(n=3)
\]  \( (1) \)

Then, the solution having the compound of formula (1) added thereto was filtered, and 0.15 mol of aluminum sulfate, 0.5 mol of boric acid, and 0.3 mol of sodium sulfate were added to the filtered solution at 70 to 80°C. These added solid elements were completely dissolved. Next, 0.5 mol of formic acid was slowly added to the solution which contained aluminum sulfate, boric acid and sodium sulfate and which was maintained at 70 to 80°C. Then, a plating bath that contained the solution having formic acid added thereto was covered with a covering member and was maintained at 70 to 80°C for approximately one hour. The solution maintained at 70 to 80°C for approximately one hour was cooled to room temperature, and distilled water was added to the cooled solution such that the volume of the plating solution became 0.9 to 0.95 L. Thereafter, a hydrogen ion index of the solution having the distilled water added thereto was measured and, if necessary, was adjusted to 1.5 by adding an H₂SO₄, NaOH, or Na₂CO₃ solution to the solution. Using a sodium lauryl sulfate \( (C_{12}H_{25}SO_4Na) \) solution prepared in a concentration of 10 g/L in advance, 0.1 g of \( C_{12}H_{25}SO_4Na \) was added to the solution having the adjusted hydrogen ion index. After the addition of \( C_{12}H_{25}SO_4Na \), the volume of the plating solution was adjusted to a final volume of 1 L using distilled water. Then, the hydrogen ion index of the solution whose volume had been adjusted to the final volume was measured again and, if necessary, was adjusted to 1.5 by adding the H₂SO₄, NaOH, or Na₂CO₃.

**Embodiment 2**

A plating solution was prepared under the same conditions as Embodiment 1, except that the hydrogen ion index was adjusted to 1.7.

**Embodiment 3**

A plating solution was prepared under the same conditions as Embodiment 1, except that the compound of formula (1) was added in an amount of 0.8 mol.

**Embodiment 4**

A plating solution was prepared under the same conditions as Embodiment 1, except that sodium sulfate was added in an amount of 0.2 mol.

**Embodiment 5**

A plating solution was prepared under the same conditions as Embodiment 1, except that the compound of formula (1) was added in an amount of 0.8 mol and that formic acid was added in an amount of 0.4 mol.

**Embodiment 6**

A plating solution was prepared under the same conditions as Embodiment 1, except that carbamide was added in an amount of 0.4 mol and that the hydrogen ion index was adjusted to 1.4.

**COMPARATIVE EXAMPLE 1**

A plating solution was prepared by adding 0.5 mol/L of chromium sulfate instead of the compound of formula (1), 0.18 mol/L of aluminum sulfate, 0.63 mol/L of sodium sulfate, 0.45 mol/L of carbamide and 0.66 mol/L of sodium formate. In addition, the hydrogen ion index was adjusted to 1.4.

**Embodiment 8**

The covering power of each of the plating solutions of Embodiments 1 through 6 and Comparative Example 1 was evaluated. Specifically, a disc electrode \((50 \text{ cm}^2)\) of a copper foil fixed to a plastic holder was used. Electroplating was conducted using TDMA at a constant current density and without the spatial separation of a cathode and an anode. The volume of the plating solution was 0.5 L. The current density was gradually increased by each 1 A/dm². Electroplating was conducted for 30 seconds for all current density values. A minimum current density when chromium was plated on the whole surface of the cathode was visually determined, and the covering power of the plating solution was measured based on...
the determination result. The measurement results are shown in Table 1. During the plating process, the temperature of a plating bath was 35°C.

<table>
<thead>
<tr>
<th>Comparative Example 1</th>
<th>22</th>
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<tbody>
<tr>
<td>Embodiment 1</td>
<td>15</td>
</tr>
<tr>
<td>Embodiment 2</td>
<td>14</td>
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<tr>
<td>Embodiment 3</td>
<td>17</td>
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<td>Embodiment 4</td>
<td>19</td>
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<tr>
<td>Embodiment 5</td>
<td>17</td>
</tr>
<tr>
<td>Embodiment 6</td>
<td>18</td>
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</tbody>
</table>

As apparent from the results shown in Table 1, the minimum current densities of the plating solutions of Embodiments 1 through 6 are far lower than that of the plating solution of Comparative Example 1. Accordingly, the plating solutions of Embodiments 1 through 6 using the trivalent chromium compound of formula (1) have better covering power than the plating solution of Comparative Example 1 using a trivalent chromium compound such as chromic sulfate.

A trivalent chromium plating solution according to the present invention has superior covering power. In addition, a compound of formula (1), which can also be used as a rusting agent, can be mass-produced and is inexpensive. Therefore, the trivalent chromium plating solution is the first ever plating solution that provides the compound of formula (1) as a trivalent chromium compound. Using the compound of formula (1) as a source, an economical trivalent chromium plating solution can be produced.

In concluding the detailed description, those skilled in the art will appreciate that many variations and modifications can be made to the preferred embodiments without substantially departing from the principles of the present invention. Therefore, the disclosed preferred embodiments of the invention are shown in a generic and descriptive sense only and not for purposes of limitation.

What is claimed is:

1. A trivalent chromium plating solution comprising:
   a trivalent chromium compound comprising a compound of formula (1) below;
   wherein $\text{Cr}_3\text{SO}_4\text{A}_\text{OH}_{3\alpha}$ (α<3) (1).

2. The plating solution of claim 1, wherein the plating solution further comprising:
   a complexing agent suppressing a polymerization reaction of the trivalent chromium compound in the plating solution;
   a conductivity agent increasing electrical conductivity of trivalent chromium ions;
   a buffer agent stabilizing a hydrogen ion index of the plating solution;
   a plating activating agent increasing adhesive power and capability of forming a plated layer;
   a wetting agent removing a pitting phenomenon which occurs on a plated surface; and
   a hydrogen ion index adjusting agent adjusting the hydrogen ion index of the plating solution.

3. The plating solution of claim 1, wherein the trivalent chromium compound is added in an amount of 0.4 to 1.3 mol/L.

4. The plating solution of claim 2, wherein the complexing agent is at least one selected from the group consisting of a formic acid, alkali metal formate and ammonium formate and is added in an amount of 0.05 to 2 mol/L.

5. The plating solution of claim 3, wherein the conductivity agent is sodium sulfate and is added in an amount of 0.1 to 0.8 mol/L.

6. The plating solution of claim 4, wherein the buffer agent comprises boric acid and aluminum sulfate, wherein the boric acid is added in an amount of 0.08 to 1 mol/L, and the aluminum sulfate is added in an amount of 0.05 to 0.2 mol/L.

7. The plating solution of claim 5, wherein the plating activating agent is carbamide and is added in an amount of 0.1 to 1.2 mol/L.

8. The plating solution of claim 6, wherein the wetting agent is sodium lauryl sulfate and is added in an amount of 0.01 to 1 g/L.

9. The plating solution of claim 7, wherein the hydrogen ion index adjusting agent may be at least one selected from the group consisting of a sulfuric acid (H$_2$SO$_4$), sodium hydroxide (NaOH), and sodium carbonate (Na$_2$CO$_3$).

10. The plating solution of claim 1, having a hydrogen ion index of 1.1 to 3.5.

11. A plating method comprising:
    preparing a trivalent chromium plating solution in a plating bath;
    immersing an object to be plated in the trivalent chromium plating solution; and
    applying a negative potential to the object to be plated and applying a positive potential to an insoluble anode after installing the insoluble anode in the plating bath, wherein the trivalent chromium plating solution comprises:
    a trivalent chromium compound comprising a compound of formula (1) below;
    a complexing agent suppressing a polymerization reaction of the trivalent chromium compound in the plating solution;
    a conductivity agent increasing electrical conductivity of trivalent chromium ions;
    a buffer agent stabilizing a hydrogen ion index of the plating solution;
    a plating activating additive increasing adhesive power and capability of forming a plated layer;
    a wetting agent removing a pitting phenomenon which occurs on a plated surface; and
    a hydrogen ion index adjusting agent adjusting the hydrogen ion index of the plating solution.

12. The plating method of claim 11, wherein the insoluble anode is a titanium-manganese dioxide anode (TMDA), a dimensionally stable anode (DSA) having iridium oxide (IrO$_2$) or ruthenium oxide (RuO$_2$) formed on a porous titanium plate, or a platinitized titanium anode.

13. The plating method of claim 11, wherein in the applying of the negative potential and applying of the positive potential, a current density is 15 to 30 A/dm$^2$.

14. The plating method of claim 11, wherein the plating bath is maintained at a temperature of 20 to 60°C.