

A NOVEL METHOD OF DECORATIVE CHROMIUM PLATING FROM TRIVALENT CHROMIUM

THE FIELD AND BACKGROUND OF INVENTION

This invention is related to a method of electroplating (or electrodeposition) of chromium and chromium alloys from baths containing trivalent chromium.

Decorative chromium plating is popularly employed in plating industries to provide a decorative plate with a desirable bright finish and corrosion resistance. Conventionally, chromium plates are electroplated from baths containing hexavalent chromium. However, many attempts over the last fifty years or so have been made to develop a commercially viable process for plating chromium using baths containing only trivalent chromium salts, as a replacement for the process using hexavalent chromium. Hexavalent chromium presents serious health and environmental hazards; it is known to cause ulcers and is believed to cause cancer. The cost of disposing hexavalent chromium plating baths and rinse water is ever increasing. Further, plating from baths containing hexavalent chromium has limited covering power and is sensitive to current interruptions, and hence its probability of producing commercially unacceptable deposits is higher. On the other hand, trivalent chromium baths have good covering power and the trivalent chromium plating process is essentially unaffected by current interruptions during the plating cycle. Most importantly, trivalent chromium compounds are much less toxic than hexavalent chromium.

Although the desirability of using trivalent chromium plating are well recognised it has not been able to supplant hexavalent chromium plating in industry despite extensive attempts to develop and improve on trivalent chromium plating processes as shown in the following summary of the prior art.

U.K.Pat.1144913 describes a trivalent chromium plating process in which the bath contains Cr(III)-dimethylformamide complexes.

U.S.Pat.3917517 describes a bath containing one or two weak complexants such as hypophosphite and glycine.

U.K.Pat.1592761 and U.S.Pat.4054494 describe a trivalent chromium plating process in which the bath contains Cr(III)-formate complexes. This trivalent chromium plating process, called Aleca-3, has been in use commercially since its introduction in 1975.

U.S.Pat.4062737 describes a trivalent chromium plating process in which the bath contains aqueous Cr(III)-thiocyanate complexes. In U.S.Pat.4161431, the above process is modified by the addition of a second complexant such as glycine, aspartic acid, formate, acetate and hypophosphite.

U.S.Pat.4278512 describes a trivalent chromium bath in which the complexant is thiocyanate but the concentration of trivalent chromium is very low, about 30 mM. The chromium deposits produced from such a bath have a lighter colour, compared to that usually obtained from a trivalent chromium bath.

U.S.Pat.4502927 and JP.Pat.55119192 describe trivalent chromium baths using an amino acid as complexant such as aspartic acid, nitrilotriacetic acid and iminodiacetic acid. Some sulphur species such as thiosulphate and thionate are also added in the baths to promote chromium deposition rate.

U.S.Pat.4053374 describes a trivalent chromium plating process in which the bath uses glycolic acid as complexant.

U.K.Pat.1602404 and U.S.Pat.4374007 describe a plating process in which the anolytes are separated from the catholytes by a perfluorinated cation exchange membrane.

This process can overcome the problems caused by the oxidation of trivalent chromium and the oxidation of other constituents of the bath at the anode.

Alternatively, in U.S.Pat.4184929, 4392922 4439285, 4477318, some additives can be oxidized at the anode in preference to trivalent chromium and other constituents.

U.S.Pat. 4432843, 5196109 suggest the use of additives which are more tolerant to the presence of one or more contaminating metal ions such as nickel, zinc, iron, copper and lead as well as organic contaminants such as excess wetting agents or brighters.

In U.S.Pat. 4612091, Benaben demonstrates a method of preparing the trivalent chromium baths. This bath is obtained by reduction of hexavalent chromium .

JP.Pat.54087643 describes a trivalent chromium plating process in which oxalic acid and its salts are used as complexants. JP.Pat.55031119 describes a trivalent chromium bath using urea or formamide as a complexant.

In order to achieve a commercially viable process of trivalent chromium plating, extensive work on trivalent chromium plating has been conducted leading to the present invention.

THE OBJECTIVES OF INVENTION

The present invention is developed in view of the above mentioned background in order to overcome the disadvantages associated with those trivalent chromium plating processes.

It is a primary objective of the present invention to provide a trivalent chromium plating process and baths for producing a bluish-white colour of trivalent chromium deposit, which is indistinguishable from the colour of hexavalent chromium deposit.

It is a further objective of the present invention to provide a trivalent chromium plating process and baths for producing a trivalent chromium deposit, which has similar physical properties as those of hexavalent chromium deposits.

It is also a further objective of the present invention to provide a trivalent chromium plating process and baths with high deposition rate and high current efficiency .

Other objectives and advantages of the present invention will be apparent from the following description.

SUMMARY OF THE INVENTION

The basis of the present invention is the unexpected discovery that by using two kinds of suitable carboxylic acids or their salts to form complexes with trivalent chromium ions, these complexes can not only produce a bluish-white colour of chromium deposit which is visually indistinguishable from the colour of hexavalent chromium deposits, but can also reach very high deposition rate and high plating efficiency.

In this invention, both the selection and the concentration of complexants are very important for obtaining a bluish-white colour of trivalent chromium deposit, fast deposition rate and high current efficiency, which are keys to the success of this trivalent chromium plating process.

According to the reports of previous literature and patents, there are many problems associated with attempts to plate chromium deposits from trivalent chromium solutions. Firstly, the deposition potential of the trivalent chromium is too negative, which results in a lot of hydrogen evolution during the chromium plating process. Secondly, with hydrogen evolution, the pH value at the electrode surface will be significantly higher than the pH in the bulk of the solution, and the chromium hydroxy species may precipitate and result in poor chromium deposits. Therefore, in order to eliminate the precipitation of the chromium

hydroxy, either stronger complexants or higher concentration of complexants may be used to generate more stable complexes, but then the chromium deposition rate will be inhibited greatly because of the stability of the chromium complexes. The choice of complexants and their concentrations must be determined by considering the following two opposing effects: a weak complexing capability may give a fast deposition rate but may result in precipitation of chromium hydroxy at the electrode surface, giving rise to poor deposits and low efficiency, whereas too strong a complexing ability will inhibit chromium plating due to excessive stability.

The present invention provides a novel method to bind and to stabilise trivalent chromium ions in the plating process by using two kinds of suitable complexants selected from carboxylic acids or their salts. Complexant I is selected from the group containing either amino-substituted carboxylic acids and their salts such as aminoacetic acid, glycine, alanine, glutamic acid and nitrilotriacetic acid, or the unsubstituted carboxylic acids and their salts such as formic acid, acetic acid, propanoic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, benzoic acid and maleic acid. Complexant II is selected from the group containing either hydroxy-substituted carboxylic acids and their salts such as glycolic acid, lactic acid, salicylic acid, malic acid, tartaric acid, citric acid, or the unsubstituted carboxylic acids and their salts as indicated above. The present invention overcomes the two opposing affects mentioned above and has two excellent advantages. Firstly, these complexants can bind trivalent chromium strongly enough to stabilise trivalent chromium against hydrolysis in the plating process, but not too strongly as to shift the deposition potential of trivalent chromium to too negative a level, *i.e.*, these complexants can enhance the trivalent chromium reduction process and also retard the hydrogen evolution reaction. Secondly, these complexants also act as auxiliary buffering agents to stabilise the trivalent chromium ions in the baths when they are released in the plating process, so less precipitation of chromium hydroxy will occur at the electrode surface. Therefore, the present invention can provide a bluish-white colour of trivalent chromium deposit, and also high deposition rate and high current efficiency can be obtained from this invention.

Thus, in this invention, the trivalent chromium solutions contain chromium sulphate or chromium chloride as a source of chromium, two kinds of different complexants selected from carboxylic acids or their salts to form complexes with trivalent chromium ions and also to act as buffering agents. Alkali metal salts are added to improve the conductivity of the solution and the current distribution in the plating process. Preferably, a buffering agent is incorporated and may comprise boric acid or soluble alkali metal borates. A wetting agent is also desirable, suitable wetting agent is sodium lauryl sulphate and triton x-100. The pH value of the solutions is maintained at between 0.5 and 5.0 and preferably at between 2.0 and 3.0. The temperature is maintained at between 25 °C and 50 °C and preferably at between 25 °C and 35 °C. A trivalent chromium deposit is electroplated by a direct current in the range of approximately 3-25 A/ dm².

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The following detailed description of the present invention illustrates the preferred embodiment.

One of its essential constituents, trivalent chromium ions can be introduced in the form of any simple aqueous soluble salts such as chromium sulphate, chromium chloride hexahydrate and chromium perchlorate. Preferably, the trivalent chromium can be introduced as chromium sulphate, which can be in the form of a cheap and readily available mixture of trivalent chromium and sodium sulphates known as tanning liquor or chrometan. The trivalent chromium concentration may range broadly from about 0.1 to 1.0 molar, and preferably from about 0.2 to 0.8 molar. When the concentration of the trivalent chromium is outside this range, the covering power of the baths is poor, and the current density region providing a desirable chromium deposit is too narrow.

The second essential constituent of the solutions is the complexants for binding the trivalent chromium ions. These two complexants can be selected from carboxylic acids or their salts and must be used in combination. Complexant I is selected from the group

containing either amino-substituted carboxylic acids and their salts such as aminoacetic acid, glycine, alanine, glutamic acid and nitrilotriacetic acid, or unsubstituted carboxylic acids and their salts such as formic acid, acetic acid, propanoic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, benzoic acid and maleic acid. Complexant II is selected from the group containing either hydroxy-substituted carboxylic acids and their salts such as glycolic acid, lactic acid, salicylic acid, malic acid, tartaric acid and citric acid, or the unsubstituted carboxylic acids and their salts as indicated above. For example, these two complexants may be selected from the following a couple of ligands such as glycine and oxalic acid, malic acid and formic acid, oxalic acid and malonic acid, citric acid and malonic acid, alanine and formic acid, and so on. The concentration of mixed complexants is controlled to provide a molar ratio of mixed complexants to trivalent chromium at about 0.5 : 1 up to about 3 : 1. When the molar ratio is smaller than 0.5, the chromium deposits are poor in brightness, coverage and adhesion. Excessive amounts of complexants are undesirable due to low deposition rate and low plating efficiency.

This trivalent chromium solution may optionally but preferably contains a buffering agent in an amount of about 0.2 molar up to its limits set by the solution solubility with amounts typically ranging up to about 1.0 molar. Preferably, the concentration of the buffering agent is controlled from about 0.6 to 1.0 molar. The use of boric acid as well as its alkali metal salts is effective to introduce borate ions into the baths which have also been found to improve the covering power of the baths.

In addition, a wetting agent may optionally but preferably be used. These wetting agents may be selected from those which are compatible and do not adversely affect the performance of the trivalent chromium solutions. Such wetting agents which can be satisfactorily employed include sodium lauryl sulphate, triton x-100 and others. The inclusion of these wetting agents has been found to contribute to the attainment of clear chromium deposits eliminating dark mottled deposits and to increase the range of current density on bright chromium deposits. The wetting agents can be employed in concentrations of up to 10 grams per litre, with amounts of about 0.05 to 2.0 g/l being preferred.

The trivalent chromium solutions may optionally but preferably contain certain amounts of conductivity salts which typically comprise salts of ammonium, alkali metals and alkaline earth metals, and strong acids such as hydrochloric acid and sulphuric acid. These conductivity salts include the sulphate salts such as ammonium sulphate, sodium sulphate and potassium sulphate, and the chloride salts such as ammonium chloride, sodium chloride and potassium chloride, and others. The inclusion of such conductivity salts is well known in this art for the purpose of increasing the conductivity of the solutions and minimising the power consumption required for chromium deposition. These salts can be used either alone or together. The concentration of these salts is not particularly restricted, being usually employed in the range of 1.0 to 3.0 molar or higher depending on the bath concentration, temperature and plating current density.

In addition to the above mentioned constituents, the solutions may optionally but preferably contain bromide such as ammonium bromide, potassium bromide and sodium bromide when the trivalent chromium solutions are to be operated directly in contact with an anode. The inclusion of bromide has been found to prevent oxidation of trivalent chromium to hexavalent chromium occurring in the plating process. The concentration of bromide in the baths may be varied within the range of 0.2 to 1.0 molar.

The trivalent chromium solutions of the above mentioned types are generally aqueous acidic solutions and contain hydrogen ions in a concentration to provide a pH on the acid side. Usually, the concentration of hydrogen ions is controlled to provide a pH value of about 0.5 to 5.0, with a pH range of about 2.0 to 3.0 being particularly satisfactory. The adjustment of the solutions to within the prescribed pH range can be achieved by the addition of any suitable acid and base compatible with the solution constituents such as hydrochloric acid, sulphuric acid, sodium hydroxide, potassium hydroxide and others.

It will be apparent from the above mentioned that a particularly preferred form of the novel electroplating solutions comprises trivalent chromium ions, a mixture of

complexants, a boric acid as a buffering agent, a wetting agent, one or a mixture of conductivity salts, and a hydrogen ion concentration to provide an appropriate pH value while the solutions are to be operated in the double-cell. In addition to the above solution constituents, a bromide will be added when the solutions are to be used in the single-cell, doing away with the need for the exchange membrane separating the anode and cathode compartments.

The solutions may conveniently be prepared by sequentially dissolving the aqueous soluble constituents in water to provide the required concentration. It is preferable to heat the solutions to about 60 °C to 90 °C, and to stir the solutions for about 30 minutes to increase the rate of dissolution of the constituents and the rate of complexing reaction between trivalent chromium ions and the mixed complexants.

The operating temperature of the trivalent chromium solutions of the present invention is preferably between 25 °C to 35 °C, and more preferably 30 °C. The current density during the plating process can range from 3 to 25 A/ dm² depending on the bath concentration, temperature, pH value and other factors. The preferred range of the current density is from 4 to 15 A/ dm².

The trivalent chromium solutions can be used both in single-cell and double-cell. There is not much difference in the colour of chromium deposits, deposition rate and plating efficiency, but it may be advantageous to separate the anode from the cathode by a cation exchange membrane for a long period use of the solutions and for the solutions containing chloride and other halides, since the exchange membrane can prevent the hexavalent chromium ions coming into the cathode compartments and can also avoid the evolution of chlorine gas during the plating process.

The trivalent chromium solutions can be used to plate chromium on conventional ferrous, nickel, stainless and brass plates. The workpieces to be chromium plated are subjected to conventional pretreatment in accordance with prevalent well-known art practices.

For anodes used in the trivalent chromium plating process, inert electrodes such as carbon electrode and platinized titanium electrode are used in the single-cell, and lead and lead alloy and platinized titanium electrode are used in the double-cell.

It is to be understood that the trivalent chromium solutions of the present invention can be used not only for decorative chromium deposit, but also for thick chromium deposit and chromium alloy deposit.

In order to further illustrate the benefits of the present invention, the following specific examples are provided. It will be understood that these examples are provided for illustrative purposes only, and are not to be construed as limiting the scope of the present invention as herein disclosed and as set forth in the appended claims.

EXAMPLES

Example 1

Constituents	Amounts of Constituents (Moles)		
	A	B	C
Chromium(III) Sulphate Basic	0.2	0.4	0.6
Glycine and Oxalic acid	0.1 - 0.6	0.2 - 1.2	0.3 - 1.8
Sodium Chloride	1.0		0.5
Potassium Chloride		1.0	0.5
Ammonium Chloride	1.0	1.0	1.0
Boric Acid	1.0	1.0	1.0
Wetting Agent (g/l)	0.05	0.05	0.05

The plating conditions (Double - Cell)

Anode : platinized titanium or lead alloy and lead

Anode electrolyte : 0.5M K_2SO_4 or 0.5M H_2SO_4

Temperature : 30 °C to 35 °C

pH value : 2.0 to 3.0

Cathode current density : 5.0 A / dm²

Cathode surface : 8.0 cm²

Plating time : 5.0 minutes

Distance between the anode and the cathode : 7.0 cm

Average thickness of the chromium deposits : 0.6 to 1.6 microns

Average deposition rate : 0.15 to 0.30 microns / min.

Plating efficiency : 20 to 32 %

Colour of the chromium deposits : bluish and white

Example 2

Constituents	Amounts of Constituents (Moles)		
	A	B	C
Chromium(III) Sulphate Basic	0.2	0.4	0.6
Malic acid and Formic acid	0.1 - 0.6	0.2 - 1.2	0.3 - 1.8
Sodium Chloride	1.0		0.5
Potassium Chloride		1.0	0.5
Ammonium Chloride	1.0	1.0	1.0
Boric Acid	1.0	1.0	1.0
Wetting Agent (g/l)	0.05	0.05	0.05

The plating conditions (Double - Cell)

Anode : platinized titanium or lead alloy and lead

Anode electrolyte : 0.5M K₂SO₄ or 0.5M H₂SO₄

Temperature : 30 °C to 35 °C

pH value : 2.0 to 3.0

Cathode current density : 5.0 A / dm²

Cathode surface : 8.0 cm²

Plating time : 5.0 minutes

Distance between the anode and cathode : 7.0 cm

Average thickness of the chromium deposits : 0.6 to 1.6 microns

Average deposition rate : 0.15 to 0.30 microns / min.

Plating efficiency : 20 to 32 %

Colour of the chromium deposits : bluish and white

Example 3

Constituents	Amounts of Constituents (Moles)		
	A	B	C
Chromium(III) Sulphate Basic	0.2	0.4	0.6
Malonic acid and Oxalic acid	0.1-0.6	0.2-1.2	0.3 -1.8
Sodium Chloride	1.0		0.5
Potassium Chloride		1.0	0.5
Ammonium Chloride	1.0	1.0	1.0
Boric Acid	1.0	1.0	1.0
Wetting Agent (g/l)	0.05	0.05	0.05

The plating conditions (Double - Cell)

Anode : platinized titanium or lead alloy and lead

Anode electrolyte : 0.5M K_2SO_4 or 0.5M H_2SO_4

Temperature : 30 °C to 35 °C

pH value : 2.0 to 3.0

Cathode current density : 5.0 A / dm²

Cathode surface : 8.0 cm²

Plating time : 5.0 minutes

Distance between the anode and the cathode : 7.0 cm

Average thickness of the chromium deposits : 0.6 to 1.6 microns

Average deposition rate : 0.15 to 0.30 microns / min.

Plating efficiency : 20 to 32 %

Colour of the chromium deposits : bluish and white

Example 4

Constituents	Amounts of Constituents (Moles)		
	A	B	C
Chromium(III) Sulphate Basic	0.2	0.4	0.6
Citric acid and Malonic acid	0.2 - 0.6	0.2 - 1.2	0.3 - 1.8
Sodium Chloride	1.0		0.5
Potassium Chloride		1.0	0.5
Ammonium Chloride	1.0	1.0	1.0
Boric Acid	1.0	1.0	1.0
Wetting Agent (g/l)	0.05	0.05	0.05

The plating conditions (Double - Cell)

Anode : platinized titanium or lead alloy and lead

Anode electrolyte : 0.5M K_2SO_4 or 0.5M H_2SO_4

Temperature : 30 °C to 35 °C

pH value : 2.0 to 3.0

Cathode current density : 5.0 A / dm²

Distance between the anode and the cathode : 7.0 cm

Cathode surface : 8.0 cm²

Plating time : 5.0 minutes

Average thickness of the chromium deposits : 0.6 to 1.6 microns

Average deposition rate : 0.15 to 0.30microns / min.

Plating efficiency : 20 to 32 %

Colour of the chromium deposits : bluish and white

Example 5

Constituents	Amounts of Constituents (Moles)		
	A	B	C
Chromium(III) Sulphate Basic	0.2	0.4	0.6
Alanine and Formic acid	0.1 - 0.6	0.2 - 1.2	0.3 - 1.8
Sodium Chloride	1.0		0.5
Potassium Chloride		1.0	0.5
Ammonium Chloride	1.0	1.0	1.0
Boric Acid	1.0	1.0	1.0
Wetting Agent (g/l)	0.05	0.05	0.05

The plating conditions (Double - Cell)

Anode : platinized titanium or lead alloy and lead

Anode electrolyte : 0.5M K_2SO_4 or 0.5M H_2SO_4

Temperature : 30 °C to 35 °C

pH value : 0.5 to 1.5

Cathode current density : 5 A / dm²

Distance between the anode and the cathode : 7.0 cm

Cathode surface : 8.0 cm²

Plating time : 5 minutes

Average thickness of the chromium deposits : 0.6 to 1.6 microns

Average deposition rate : 0.15 to 0.30 microns / min.

Plating efficiency : 20 to 32 %

Colour of the chromium deposits : light and white

Example 6

The same solutions as given in Example 3 are prepared but with the addition of some bromide such as ammonium bromide and potassium bromide, and chromium plating is carried out in the process which does away with the need for the exchange membrane separating the anode from cathode compartments. Satisfactory chromium deposits are obtained at the same plating conditions as given in Example 3. The colour and thickness of chromium deposits, deposition rate and plating efficiency are nearly the same as those in Example 3.

While we have described preferred embodiments of our invention, it is to be understood that we do not limit ourselves to these precise disclosures and reserve the right of all changes and modifications covered within the scope of the invention as defined in the appended claims.

CLAIMS

1. An aqueous acidic trivalent chromium electroplating solution containing essentially trivalent chromium ions, water soluble mixed complexants for maintaining the trivalent chromium ions stable in solution, a buffering agent, a wetting agent, conductivity salts and hydrogen ions to provide a pH on the acid side.
2. The electroplating solution as defined in Claim 1 in which said trivalent chromium ions are present in an amount of about 0.1 to 1.0 molar.
3. The electroplating solution as defined in Claim 1 in which the mixed complexants are made up of two kinds of carboxylic acids or their salts. Complexant I is selected from the group containing either amino-substituted carboxylic acids and their salts such as aminoacetic acid, glycine, alanine, glutamic acid and nitrilotriacetic acid, or unsubstituted carboxylic acids and their salts such as formic acid, acetic acid, propanoic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, benzoic acid and maleic acid. Complexant II is selected from the group containing either hydroxy-substituted carboxylic acids and their salts such as glycolic acid, lactic acid, salicylic acid, malic acid, tartaric acid and citric acid, or the unsubstituted carboxylic acids and their salts as indicated above.
4. The electroplating solution as defined in Claim 1 in which said mixed complexants are present in a molar ratio of mixed complexants to trivalent chromium from about 0.5 : 1 to 3 : 1.
5. The electroplating solution as defined in Claim 1 in which the buffering agent is boric acid or its alkali metal salts.
6. The electroplating solution as defined in Claim 1 in which said borate ions are present in an amount of about 0.2 to 1.0 molar.
7. The electroplating solution as defined in Claim 1 in which the wetting agents are sodium lauryl sulphate or triton x - 100 .
8. The electroplating solution as defined in Claim 1 in which said wetting agents are present in an amount of about 0.05 to 10 g / l.
9. The electroplating solution as defined in Claim 1 in which the conductivity salts are ammonium salts, alkali metal salts and alkaline earth metal salts.



10. The electroplating solution as defined in Claim 1 in which said conductivity salts are present in an effective amount up to the solubility limit thereof in the solution.
11. The electroplating solution as defined in Claim 1 in which said hydrogen ions are present to provide a pH value of about 0.5 to 5.0.
12. The electroplating solution as defined in Claim 1 in which said trivalent chromium ions are present in an amount of about 0.1 to 1.0 molar, said mixed complexants are present in a molar ratio of mixed complexants to trivalent chromium of about 0.5 : 1 to 3 : 1, said borate ions are present in an amount of about 0.2 to 1.0 molar, said wetting agent is present in amount of about 0.05 to 10 g / l , said conductivity salts are present in an effective amount up to the solubility limit thereof in the solution, and said hydrogen ions are present to provide a pH value about 0.5 to 5.0 .
13. A trivalent chromium electroplating bath comprising an anolyte separated from an aqueous acidic trivalent chromium catholyte by a perfluorinated cation exchange membrane, and the catholyte consisting of a source of trivalent chromium ions, a mixture of complexants, a buffering agent, a wetting agent, conductivity salts and hydrogen ions to provide a pH value of about 0.5 to 5.0 and maintained at a temperature of about 25°C to 50°C.
14. The bath as claimed in Claim 13 in which the anolyte contains sulphate ions in an amount of about 0.5 to 2.0 molar.
15. The bath as claimed in Claim 13 in which the anode is lead, lead alloy or platinized titanium .
16. The bath for trivalent chromium electroplating characterised by a single plating cell containing the electrolyte as defined in claims 1 to 12 and to which is added a bromide to prevent the oxidation of trivalent chromium to hexavalent chromium at the anode surface.
17. The bath as claimed in Claim 16 in which the said bromide may be potassium bromide, ammonium bromide or sodium bromide in an amount of about 0.2 to 1.0 molar.
18. A process for electroplating chromium on a cathode which comprises the steps of immersing a cathode to be deposited in the bath as defined in claims 13 to 17, applying an electrical current between an anode and said cathode to provide a current



density of about 4 to about 15 A/dm² for a period of time to deposit the required thickness of chromium on said cathode.