

# PATENT SPECIFICATION

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## (54) CHROMIUM ELECTROPLATING

(71) We, ALBRIGHT & WILSON LIMITED, a British Company of Albright & Wilson House, Hagley Road West, Oldbury, Warley, West Midlands, do hereby declare the invention, for which we pray that a Patent may be granted to us and performed to be particularly described in and by the following statement:—

The present invention relates to chromium electroplating, and in particular to the maintenance of electroplating baths based on trivalent chromium.

Although the potential advantages of electroplating from solutions containing chromium in the trivalent state have been recognised for over fifty years, until recently a variety of practical difficulties have prevented the commercial adoption of any such solution. Chromium has therefore always been electroplated from baths containing the chromium in the hexavalent state, despite certain serious disadvantages of such baths.

Recently, however, various proposals have been made for overcoming at least some of the aforesaid difficulties. One type of bath in particular, containing a trivalent chromium salt, a formate, a bromide and ammonium as essential ingredients is described in our U.S. Patent No. 3,954,574. A process based on such a bath has recently been introduced commercially and is already gaining widespread acceptance as a replacement for hexavalent chromium plating baths.

However, it has been discovered that some trivalent chromium plating baths, which work satisfactorily under laboratory or test conditions, sometimes develop plating defects after they have been installed commercially. In particular at least one, and usually a combination, of the following plating faults may occur:

- A. A white haze at high current densities, which may, in severe cases, spread progressively to lower current densities.  
 B. A white band at the lower limit of the plating range, often accompanied by

loss of adhesion at high current densities. 50

C. A white deposit at current densities of around 50 amps per square foot.

D. Brown or black smudges between about 100 and 200 amps per square foot. 55

We have now discovered that the aforesaid faults may, in many cases, be reduced or overcome by adding a small amount of water soluble ferrocyanide to the plating solution, whenever the faults are observed. 60

Our invention therefore provides a method for the maintenance of an aqueous trivalent chromium electroplating bath which has begun to exhibit at least one of the aforesaid plating faults, which comprises adding thereto an amount of a water soluble ferrocyanide sufficient substantially to reduce or eliminate said plating fault. 65 70

We have found that the invention is applicable to the maintenance of trivalent chromium electroplating baths generally. For example it may be employed with baths of the type described in our aforesaid U.S. patent, or with baths containing glycollic acid such as are described in USP 3706636 to 643. The invention may also be used, for example, in combination with baths of the type described in BP 1144913, USP 3021267, USP 3006823, USP 3069333 and USP 3111464. 75 80

Generally speaking the baths contain a trivalent chromium salt, such as chromium chloride, sulphate or fluoride and a complexing agent such as a carboxylic acid, preferably a formate, or alternatively, for example, an acetate, glycollate or oxalate. Halides especially bromide are preferably present. The solution preferably contains alkali metal ions, for example sodium and/or potassium, and sulphate ions. Aprotic dipolar solvents such as dimethyl formamide may also be included but are preferably absent. Typically the pH of the bath is between 1 and 7, for example 1.5 to 5. 85 90 95

The ferrocyanide may be any

ferrocyanide which is soluble in the bath, for example an alkali metal or ammonium ferrocyanide, for example sodium or potassium ferrocyanide.

The ferrocyanide may conveniently be added to the bath as an aqueous solution. The concentration of the ferrocyanide solution is not critical, and will normally be chosen according to the solubility of the particular ferrocyanide employed. For example using potassium ferrocyanide we prefer to employ a solution containing about 20% by weight ferrocyanide.

We have found that addition of ferrocyanide in amounts in excess of those required to eliminate the aforesaid faults, may cause a deterioration in the performance of the bath. One way of avoiding this problem when the onset of any of the aforesaid faults is observed, is to add the ferrocyanide solution in small increments until the chromium deposit is satisfactory again. If a sufficient excess of ferrocyanide has accidentally been added to cause a significant deterioration, it is possible to remove the excess by adding a small amount of soluble cation such as copper, nickel, iron or zinc. In most plating shops this may conveniently be achieved by adding a small amount of nickel plating solution to the bath. The addition of metal ion should be made within 15 minutes preferably within 10 minutes of adding the ferrocyanide, in order to be fully effective, since on standing the excess ferrocyanide complexes with the chromium and is then difficult or impossible to precipitate with the added metal.

We believe that the aforesaid faults may be due to the accidental contamination of the bath by traces of metal cations, which are capable of codepositing with the chromium. Our experiments have shown that fault A can be simulated by adding copper to the bath; similarly fault B appears to be associated with the presence of zinc, fault C with lead and fault D with iron or nickel. It seems, surprisingly, that the ferrocyanide is capable of precipitating substantially all of the potentially harmful trace metals which are most commonly encountered in very low concentrations as contaminants in commercial practice, but without precipitating the chromium, which is a principal cationic constituent of the bath.

According to a preferred embodiment, therefore our invention provides a method of maintaining an aqueous trivalent chromium electroplating bath which exhibits plating defects associated with the codeposition with the chromium of trace metal contaminants, which method comprises determining the concentration of said trace metal contaminants

precipitable by ferrocyanide in the bath and adding a water soluble ferrocyanide in an amount sufficient to precipitate said contaminants.

Preferably the bath or any sample used for analysis should be filtered to remove any previously precipitated metal prior to the analysis.

The analysis of the bath may be carried out by any of the analytical techniques for quantitative determination of the trace metals which are well known in the art. Typically the bath may be analysed by spectographic means, for example by spark ionisation or atomic absorption. Alternatively polarographic means may be employed.

Usually it is only necessary to test for copper, zinc, iron and nickel, since these are the only metals which in our experience, are likely to cause said plating faults. The invention is however applicable to the correction of plating faults due to the presence of other codepositable metals, including lead, cadmium, silver, and gold, although significant contamination by such metals is unlikely to occur in practice.

The amount of ferrocyanide added is preferably substantially stoichiometric based on the trace metal contaminants present, or slightly less. Any substantial excess of ferrocyanide should be avoided. Addition of any effective quantity significantly less than the stoichiometric amount, while beneficial, may not entirely remove the plating fault. We have discovered that a good rule of thumb is to add 1 ml. of 20% potassium ferrocyanide solution per litre of plating solution for every 50 ppm of trace metal contamination. In this way the bath can be relatively easily maintained in the face of at least the commonly encountered forms of contamination.

It is preferred to reduce any free halogen in the bath to halide prior to addition of the ferrocyanide, by addition of a reducing agent capable of converting halogen to halide, without adversely affecting the performance of the bath. One particularly suitable reducing agent for this purpose is ammonium formate. The proportion of formate is preferably sufficient to reduce all the free halogen in the solution. Typically 2 to 3 gms per litre of formate may be added, preferably as an aqueous solution. The formate is preferably added with agitation, about 10 minutes prior to the ferrocyanide addition. Halogen is usually present in the bath immediately after plating.

The invention will be illustrated by the following Examples:

#### Example 1

An aqueous trivalent chromium plating

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solution which had been working satisfactorily developed a plating fault, giving dark smudges in the 100—200 ASF region. A sample of the solution was put into a 300 ml Hull Cell with circulatory cooling and a 10 amp 3 minute panel run. This showed black streaks between 100—200 ASF and from previous experience was diagnosed as being due to nickel and possibly iron contamination of the solution. It was established that some nickel plated components had been lost from plating jigs and had been dissolving in the electrolyte for some time. The electrolyte was analysed spectroscopically for trace metals as follows:—

|               |         |
|---------------|---------|
| Nickel        | 134 ppm |
| Copper        | 13 ppm  |
| Iron          | 193 ppm |
| Zinc          | 26 ppm  |
| Total Metals: | 366 ppm |

A 20%w/v solution of potassium ferrocyanide ( $K_4Fe(CN)_6 \cdot 3H_2O$ ) was prepared and 1 ml of this solution added per 50 ppm total metals per litre i.e. 7 ml per litre were actually added. The mixture was allowed to stand for 30 minutes and then used for plating components. The black streaks were completely absent and normal plating performance was regained.

Subsequent analysis of the electrolyte gave the following result:—

|        | ppm | %removal |
|--------|-----|----------|
| Nickel | 20  | 85       |
| Iron   | 98* | (49)     |
| Copper | 4   | 69       |
| Zinc   | 8   | 69       |

\*this figure will include a contribution from any excess reagent.

Example 2

A similar electrolyte contaminated with iron, nickel, copper and zinc gave plating faults. In this case no trace metal analysis was available. Halogen was reduced by addition to the bath of 5 ml/litre of 55% w/w ammonium formate solution. The bath was agitated for 10 minutes, and then 20% potassium ferrocyanide was added in a stepwise fashion, beginning with 1 ml per

litre of electrolyte and increasing the addition in 1 ml per litre steps, allowing 30 minutes reaction time between additions. Some improvement was noted after the addition of 3 ml per litre and fully satisfactory performance was achieved at 5 ml per litre. The precipitate of insoluble metal salts was allowed to remain in the bath and did not interfere with plating in any way, but the solution was filtered at the next shutdown to remove the precipitated metals.

WHAT WE CLAIM IS:—

1. A method for the maintenance of an aqueous trivalent chromium electroplating bath which has begun to exhibit at least one of the plating faults as specified herein which comprises adding thereto an amount of a water soluble ferrocyanide sufficient substantially to reduce or eliminate said plating fault.

2. A method according to Claim 1 wherein said water soluble ferrocyanide is sodium, potassium or ammonium ferrocyanide.

3. A method for the maintenance of an aqueous trivalent chromium electroplating bath which comprises determining the proportion of trace metal contaminants therein precipitable by ferrocyanide and adding thereto sufficient of a water soluble ferrocyanide to precipitate said trace metals.

4. A method according to Claim 3 wherein an excess of said ferrocyanide is added to said bath and said excess is subsequently removed by adding thereto sufficient of a trace metal to precipitate said excess.

5. A method according to any foregoing claim wherein any free halogen present in the bath is reduced to halide prior to the addition of the ferrocyanide.

6. A method for the maintenance of an aqueous trivalent chromium electroplating bath according to any of claims 1 to 5 substantially as described herein in any of the examples.

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5 region. A sample of the solution was put  
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This showed black streaks between 100—200  
10 ASF and from previous experience was  
diagnosed as being due to nickel and  
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It was established that some nickel plated  
components had been lost from plating jigs  
and had been dissolving in the electrolyte  
for some time. The electrolyte was analysed  
15 spectroscopically for trace metals as  
follows:—

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|    | Copper        | 13 ppm  |
|    | Iron          | 193 ppm |
| 20 | Zinc          | 26 ppm  |
|    | Total Metals: | 366 ppm |

A 20%w/v solution of potassium  
ferrocyanide ( $K_4Fe(CN)_6 \cdot 3H_2O$ ) was  
25 prepared and 1 ml of this solution added per  
50 ppm total metals per litre i.e. 7 ml per  
litre were actually added. The mixture was  
allowed to stand for 30 minutes and then  
used for plating components. The black  
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plating performance was regained.

Subsequent analysis of the electrolyte  
gave the following result:—

|    |        |     |          |
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|    |        | ppm | %removal |
|    | Nickel | 20  | 85       |
| 35 | Iron   | 98* | (49)     |
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#### 40 Example 2

A similar electrolyte contaminated with  
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addition of 3 ml per litre and fully  
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ml per litre. The precipitate of insoluble  
metal salts was allowed to remain in the  
bath and did not interfere with plating in  
any way, but the solution was filtered at the  
60 next shutdown to remove the precipitated  
metals.

#### WHAT WE CLAIM IS:—

1. A method for the maintenance of an  
aqueous trivalent chromium electroplating  
bath which has begun to exhibit at least one  
of the plating faults as specified herein  
which comprises adding thereto an amount  
65 of a water soluble ferrocyanide sufficient  
substantially to reduce or eliminate said  
plating fault.

2. A method according to Claim 1  
70 wherein said water soluble ferrocyanide is  
sodium, potassium or ammonium  
ferrocyanide.

3. A method for the maintenance of an  
aqueous trivalent chromium electroplating  
bath which comprises determining the  
proportion of trace metal contaminants  
therein precipitable by ferrocyanide and  
80 adding thereto sufficient of a water soluble  
ferrocyanide to precipitate said trace  
metals.

4. A method according to Claim 3  
wherein an excess of said ferrocyanide is  
added to said bath and said excess is  
subsequently removed by adding thereto  
sufficient of a trace metal to precipitate said  
85 excess.

5. A method according to any foregoing  
claim wherein any free halogen present in the  
bath is reduced to halide prior to the  
addition of the ferrocyanide.

6. A method for the maintenance of an  
aqueous trivalent chromium electroplating  
bath according to any of claims 1 to 5  
95 substantially as described herein in any of  
the examples.

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