(51) International Patent Classification 6 : C25D 3/02

(11) International Publication Number: WO 98/18982

(43) International Publication Date: 7 May 1998 (07.05.98)

(21) International Application Number: PCT/BR97/00062

(22) International Filing Date: 31 October 1997 (31.10.97)

(30) Priority Data:
    PI 9605389–5 31 October 1996 (31.10.96) BR


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Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: AN ALKALINE ELECTROLYTIC BATH AND A PROCESS FOR ELECTRODEPOSITION OF Cu, Zn, OR Ni, AS WELL AS THEIR ALLOYS

(57) Abstract

The present invention refers to an electrolytic bath for deposition of Cu, Zn, or Ni, as well as their alloys, the bath being free from cyanide, containing at least one source of the metal or alloy to be deposited and a complexing agent, wherein a combination of at least one aliphatic amine and a quinone being used as the complexing agent combination. The invention also relates to a process for electrodeposition of Cu, Zn, or Ni, as well as their alloys, in which an electrolytic bath free from cyanide, containing at least one source of the metal or alloy to be deposited and a complexing agent comprising a combination of at least one aliphatic amine and a quinone is used.
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Field of the Invention

The present invention refers to alkaline electrolytic baths which can be used for electrodeposition of metals and metallic alloys onto equally metallic surfaces, said baths being free from cyanides.

Background of the Invention

In view of the increasing need for less harmful materials, which reduce the environment contamination, experts have been trying to develop electrolytic baths which are free from cyanide ion, because this is an extremely toxic product.

Various compositions for electrodeposition baths are known, which replace the cyanide ion by other compounds capable of providing good results with regard to the quality of the final metallic layer. These compounds include some aliphatic amines which are already cited in documents of the prior art as being a component suitable for preparing electrolytic baths free from cyanide.

US Document 4,889,602, for example, describes an electrolytic bath for deposition of a zinc-nickel alloy coating, which comprises aliphatic amines in its composition. According to the bath claimed in this document, the composition thereof should contain an electrolyte selected from the group consisting of alkaline hydroxides, and its pH value should necessarily be above 11, to provide the desired results.

Also the US patent document with publication number H1136 presents an electrolytic solution for deposition of silver, which comprises, as essential components, an aliphatic amine and an alkaline hydroxide.

Still other documents of the prior art already describe the use of aliphatic amines in electrolytic baths, which, however, should be complexed or stabilized with determined specific compounds to avoid the adverse effect of formation of a salt
precipitate of the metal to be deposited, which tends to accumulate in the electrolytic
bath and consequently impair the final result.

This is the case of JP 61006997, which discloses an electrolytic bath free from
cyanide which, in addition to the source compound of the metal to be deposited and
other compounds, for example, triethanolamine, also comprises sulfamic acid or its salt
as a stabilizing compound. Documents US 5,302,278 and JP 54,155,132 describe bath
compositions for electrodeposition of monovalent metals containing aliphatic amines
together with thiosulphate and an organic sulfinate stabilizer.

Another document which foresees the use of aliphatic amines in electrolytic
baths free from cyanide ions is US 5,538,617. This document claims the use of
compounds such as diethyl hydroxylamine as an additive specifically for halogenated
electrolytic solutions for electrodeposition of tin. The amine may be used either alone
or in combination with other compounds such as, for example, hydroquinone. However, the bath described in the mentioned US document is clearly indicated for
specific electrodeposition of tin, and there is no other mention of the possibility of
using or even adapting the bath composition defined therein so as to enable the use
thereof for electrodeposition of other metals or metallic alloys. In addition, figures 6
and 7 make it clear that, even though the various additives mentioned therein can be
used either alone or combined with each other, the recent studies carried out by the
inventors of that composition have reached the conclusion that the most effective
combination, which effectively would present a synergetic effect, would comprise
hydroquinone and citric acid.

Document JP 57002890 describes a stabilizer for electrodeposition baths of gold
selected, among others, from amines or, alternatively, hydroquinone. On the other
hand, document US 5,145,572 refers to the pre-treatment of a catalytically activated
metallic surface, prior to the step of electrodepositing metal, in which one uses organic
compounds containing nitrogen such as aliphatic amines, or non-nitrogenated
compounds, for example, hydroquinone.

The use of quinones associated with electrolytic solutions is already known
from other documents of the prior art. Document US 5,021,135 describes a method for
treating spent electrolytic baths by employing hydroquinone as a chelating agent, which will react with the metal ions that contaminate such baths. After addition of the chelating agent, the contaminated solutions are subjected to filtration and ion-exchange processes, and then return to the bath proper.

Still other solutions for specific electrodeposition of Sn, Ag, Pb and Au are known, which contain hydroquinone, which, however, should be associated to determined specific compounds that are always essential to provide the preparation of a coating of said metals.

Summary of the Invention

The present invention refers to an alkaline bath for electrodeposition of Cu, Zn or Ni, as well as their alloys, said baths being free from cyanide, containing at least one source of metal or alloy to be deposited and a complexing agent wherein a combination of at least one aliphatic amine and a quinone is used as the complexing agent.

Another embodiment of the invention is a process for electrodeposition of Cu, Zn or Ni, as well as their alloys, comprising the use of an electrolytic bath free from cyanide, containing at least one source of the metal or alloy to be deposited and a complexing agent which comprises a combination of at least one aliphatic amine and one quinone.

Detailed Description of the Invention

The electrolytic bath composition of the present invention is suitable for the electrodeposition of Ni, Zn, Cu, or their alloys onto any metallic surface. It has been surprisingly found that the complexing effect of the aliphatic amines, when used in baths for electrolytic deposition of the mentioned metals, in replacement of cyanide ions, can be improved by the simultaneously use of quinones.

Such complexing effect, as defined herein, relates to the reaction of the aliphatic amine with the metalsource-compounds in question, thus preventing them from remaining free to form salts with the ions of the electrolyte present, which reduce the electrolytic power of the bath as a whole. The quinone, in turn, increases and stabilizes this complexing power, causing the combination of these compounds to present a much better effective result than it would happen if they were used either alone or in
combination with other compounds known from the prior art. The aliphatic amine together with the quinone reduces the so-called chemical "drag out" of the source-metals, thus increasing the durability of the bath, without the need of using any other compounds stabilizing the electrolytic composition.

For the purposes of the invention, one or more aliphatic amines are used, preferably mono-, di- or triethanolamine is used, more preferably monoethanolamine is used. For combination with the aliphatic amine, the preferably used quinone is hydroquinone.

The complexing agent, that is to say, the aliphatic amine/quinone combination is advantageously used so as to provide a total amount ranging from 1 to 100 g/L, based on the total volume of the bath, preferably from 10 to 100 g/L, and more preferably from 20 to 60 g/L. Generally the weight amine/quinone ratio lies preferably in the range from 10,000/1 to 100/1.

The solution described herein is ideal for baths of electrodeposition of Zn, Cu and Ni, as well as their alloys and, as the source of these metals or alloys, any compound that is conveniently employed for this purpose can be used, such as sulphates, carbonates, chlorides, or oxides. Depending upon the specific metal or alloy to be deposited, hydrated nickel sulphate, nickel carbonate, copper (II) chloride, hydrated copper sulfate, zinc oxide, hydrated zinc sulphate, or zinc carbonate are preferably used. Among them, the preferred ones are hydrated nickel sulphate, copper (II) chloride and zinc oxide. The amounts of the metal source compounds in the composition will be determined according to each particular bath, but usually they should be within the range which provides from 0.1 to 50 g/L of the metal, based on the total volume of the bath, preferably between 1 and 50 g/L, and more preferably from 5 to 20 g/L.

Of course, the electrolytic bath described herein also contains current-conducting components, which, however, are conventional and non-determinant of the invention; they can be chosen, for instance, from the group consisting of carbonates, bicarbonates, hydroxides, and chlorides. Preferably, either bicarbonates or chlorides are used, and more preferably they are selected from sodium bicarbonate or
ammonium chloride. These electrolytes are usually employed in concentrations ranging from 1 to 80 g/L of bath, preferably from 1 to 20 g/L.

In addition to the metal source compounds, the complexing aliphatic amine/quinone combination and the electrolyte, the electrolytic bath of the invention may contain other conventional additives, which may be promptly selected by any person skilled in the art, depending upon the particular desired results.

In a particularly preferred embodiment, the electrolytic bath composition of the invention further comprises a soluble gluconate salt. The gluconate enhance the complexing power of the bath, reacting with the metal source compounds which may possibly not react with the amine and still remain free. The soluble gluconate salt may be selected, for example, from either sodium gluconate or potassium gluconate and may be used in a concentration ranging from 0 to 300 g/L, based on the total volume of the bath, and more preferably from 50 to 150 g/L. The addition of gluconate is particularly useful when the electrolytic baths according to the invention are employed for electrodeposition onto substrates of zinc and its alloys.

When the electrolytic bath is used for deposition of a decorative layer of zinc, the use of the complexing combination according to the invention provides excellent results in the final colorpattern and in the deposition rate, without the disadvantages of the baths previously known. For example, there is no need for using either alkaline hydroxides or pyrophosphates in the electrolyte, which represents a considerable technical advance, since the former prevent the utilization of this type of bath for deposition of nickel onto zinc alloys of the “zamac” type, due to the high pH value they impart to the baths, whereas the pyrophosphates are known to be toxic. The present electrolytic composition still has the advantage of providing a longer useful life, even in the case of a later brass application, since copper and zinc ions which are also present in the brass and which are trailed into the bath during the brass application do not function as contaminants of the process if the present complexing agent is used. A preferred bath for electrodeposition of Ni comprises from 1 to 50 g/L of nickel used as hydrated nickel sulphate, from 20 to 100 g/L of aliphatic amine and from 0.01 to 0.1 g/L of hydroquinone and from 1 to 2 g/L of ammonium chloride. It is further possible
to obtain a graphite-color tonality by adding from 0.1 to 1 g/L of zinc oxide, all of the concentrations mentioned herein being based on the total volume of the bath.

Electrolytic baths for deposition of copper are also advantageously obtained in accordance with the invention. By using a complexing agent which combines aliphatic amine and quinone, a composition is obtained the metal contents of which are lower than in the baths treated with a cyanide, thus providing less drag out of chemical products to washing waters. This bath also enables the use of brightening additives, such as, for example, EDTA, which enhances the brightness and leveling of the base material. In a preferred embodiment, the alkaline bath of copper comprises from 5 to 20 g/L of copper as copper (III) sulphate, from 20 to 60 g/L of aliphatic amine, from 0.02 to 0.2 g/L of hydroquinone and from 20 to 80 g/L of sodium hydroxide, all the concentrations being based on the total volume of the bath.

In another embodiment, the invention relates to a process for electrodeposition of Cu, Zn, or Ni, as well as their alloys, which one comprises the use of an alkaline electrolytic bath free from cyanide containing at least one source of the metal or alloy to be deposited and a complexing agent which comprises the combination of at least one aliphatic amine and one quinone. In this process there is no limitation as to the type of equipment or process parameters, such as types of anode, density of current, pH, etc., which are those conveniently employed and can be determined by those skilled in the art.

Generally, the electrolytic solutions of the present invention have a longer useful life and higher deposition rate, if compared with solutions which use only one of the above-mentioned components. In addition, the baths as now claimed provide greater color stability of the deposited layer, permit greater control of the process parameters and, of course, have the considerable advantage of being less harmful to the environment, since they do not utilize highly toxic compounds such as cyanide ion.

Another advantage achieved with the present invention is the considerable reduction of costs with the preparation and maintenance of the electrolytic compositions, since it enables the use of metal source compounds and of less
expensive electrolytes than those which used to be necessarily employed for each type of bath.

The invention will be better illustrated by the examples given below.

Example 1 - Decorative Nickel Bath with Graphite-Color Tonality

An electrolytic bath was prepared with hydrated nickel sulphate providing 5 g/L of Ni\(^{2+}\), based on the total volume of the bath. 40 g/L of monoethanolamine and 0.01 g/L of hydroquinone were added. In addition, ammonium chloride in a concentration of 2 g/L and 10 g/L of sodium bicarbonate were used. The pH was maintained within a range of 9.5 and 10.5 and electrolytic nickel anodes were employed in the operation, using a current density of 0.5 A/dm\(^2\). The bath was maintained at room temperature under air stirring. To obtain a graphite-coloration 0.4 g/L of ZnO was added.

It was found that the above composition can be employed as a reinforcement in a cyanide-based bath, enabling the transformation thereof into a cyanide-less bath.

Comparative Example 1

A bath for electrodeposition of nickel with graphite-color tonality was prepared in the same way as in example 1, except for the monoethanolamine and the hydroquinone, which were replaced with an amount of 20 g/L of sodium cyanide together with 2 g/L of sodium pyrophosphate.

The results obtained during the operation of the two baths are shown in comparative table 1:

**TABLE 1**

<table>
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<tr>
<th>Characteristic</th>
<th>Example 1 (without cyanide)</th>
<th>Comparative Example 1; (with cyanide)</th>
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<td>1) color pattern</td>
<td>more homogeneous</td>
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2) deposition time  
   (medium size rectangular piece)  
   7.5 min. 10 min

3) Useful life  > 8 months 6 months

4) Anodes without passivation with passivation
5) Pyrophosphates absent necessary
6) Toxicity low high

The data of Table 1 clearly indicate that during the operation of the bath prepared in accordance with the invention, the anodes do not polarize and the achieved color pattern, as well as other deposition parameters, were regarded as improved with respect to those achieved with a bath treated with cyanide.

Example 2 - Alkaline Copper Bath

An electrolytic bath was prepared by adding copper (II) sulphate so as to provide a Cu\(^{0}\) content of 10 g/L based on the total bath. 20 g/L of monoethanolamine and 0.02 of hydroquinone were added. Also sodium hydroxide was used in a concentration of 60 g/L. The process of copper electrodeposition was carried out by employing electrolytic copper anodes and a current density of 1.0 A/dm\(^2\). The bath was maintained at room temperature under mechanical stirring and continuous filtration.

The resulting electrolytic composition enabled the deposition of a layer of copper of excellent quality and brightness superior than that of alkaline baths treated with cyanide.

Example 3 - Alkaline Copper Bath for Electrodeposition onto Zinc Alloys (Ex.: Zamac)

An electrolytic bath was prepared by adding copper (II) sulphate so as to provide a Cu\(^{0}\) content of 20 g/L based on the total bath. 10 g/L of triethanolamine, 0.02 g/L of hydroquinone and 100 g/L of sodium gluconate were added. Also sodium
hydroxide in a concentration of 20 g/L was used. The process of copper electrodeposition was carried out by employing electrolytic copper anodes and a density of current of from 1.0 to 2.0 A/dm². The bath was maintained at 50° C under mechanical stirring and continuous filtration.

The resulting electrolytic composition enabled the deposition of a layer of copper of excellent quality and with high brightness.

Example 4 - Transformation of a Cyanidic Brass Bath into a non-Cyanidic one

To a brass bath containing the following composition:

\[ \text{Zn}^0 = 10 \, \text{g/L in the form of zinc cyanide} \]
\[ \text{Cu}^0 = 10 \, \text{g/L in the form of copper cyanide} \]
\[ \text{NaCN (free)} = 5 \, \text{g/L} \]
\[ \text{NaCN (total)} = 25 \, \text{g/L} \]
\[ \text{Na}_2\text{CO}_3 = 10 \, \text{g/L} \]

a mixture of 2 L of monoethanolamine + 0.02 g of hydroquinone was added daily until the washing waters did not show the presence of cyanide any longer.

The concentrations of Cu⁰ and Zn⁰ were maintained by means of electrolytic copper and zinc anodes and, when necessary, by adding either copper (II) chloride or ammoniacal zinc dissolved in monoethanolamine, to maintain the concentrations of copper and zinc at about 10 g/L.

This procedure enabled the deposition of brass without contamination of the washing waters with cyanide in contents higher than 0.2 g/L, which is the maximum contents permitted by the legislation in force in Brazil.
CLAMS

1- An alkaline electrolytic bath for deposition of Cu, Zn, or Ni, as well as their alloys, said bath being free from cyanide, containing at least one source of the metal or alloy to be deposited and a complexing agent, characterized in that a combination of at least one aliphatic amine and one quinone is used as the complexing agent.

2- An electrolytic bath according to claim 1, characterized in that said at least one aliphatic amine is selected from the group comprising mono-, di- or triethanolamine.

3- An electrolytic bath according to claim 2, characterized in that said at least one aliphatic amine is monoethanolamine.

4- An electrolytic bath according to claim 1, characterized in that said quinone is hydroquinone.

5- An electrolytic bath according to any one of claims 1 through 4, characterized in that said complexing agent is used in a proportion of from 1 to 100 g/L, based on the total volume of the bath.

6- An electrolytic bath according to any one of claims 1 to 5, characterized in that the weight ratio of the aliphatic amine and the quinone ranges from 10,000/1 to 100/1.

7- An electrolytic bath according to any one of claims 1 to 6, characterized in that said at least one source of metal or alloy to be deposited is selected from the group comprising carbonates, sulphates, chlorides and oxides of said metals.

8- An electrolytic bath according to any one of claims 1 to 7, characterized in that it further contains at least one electrolyte selected from the group comprising carbonates, bicarbonates, chlorides and hydroxides.

9- An electrolytic bath according to claim 8, characterized in that the electrolyte is chosen from sodium bicarbonate and ammonium chloride.

10- An electrolytic bath according to any one of claims 1 to 9, characterized in that it further contains at least one gluconate salt.
11- An electrolytic bath according to claim 10, characterized in that the gluconate salt is selected from either sodium gluconate or potassium gluconate.

12- An electrolytic bath according to claim 10 or 11, characterized in that the gluconate salt is used in a concentration ranging from 0 to 300 g/L, based on the total volume of the bath.

13- An electrolytic bath according to any one of claims 1 to 12, characterized in that it is used for electrodeposition of nickel and that it comprises hydrated nickel sulphate as a source compound to provide from 1 to 50 g/L of Ni⁰, from 20 to 100 g/L of monoethanolamine, from 0.01 to 0.1 g/L of hydroquinone and from 1 to 2 g/L of ammonium chloride, all concentrations being based on the total volume of the bath.

14- An electrolytic bath according to claim 13, characterized in that it further contains from 0.1 to 1.0 g/L of zinc oxide, based on the total volume of the bath.

15- An electrolytic bath according to any one of claims 1 to 12, characterized in that it is used for electrodeposition of copper and that it contains copper (II) sulphate providing from 5 to 20 g/L of Cu⁰, from 20 to 60 g/L of monoethanolamine, from 0.12 to 0.2 g/L of hydroquinone and from 20 to 80 g/L of sodium hydroxide, all concentrations being based on the total volume of the bath.

16- A process for electrodeposition of Cu, Zn, or Ni, as well as their alloys, characterized in that it comprises the use of an electrolytic bath as defined in any one of claims 1 to 15.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6  C25D3/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6  C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>A</td>
<td>US 5 538 617 A (STEINBICKER RICHARD N ET AL) 23 July 1996 cited in the application</td>
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<td>Section Ch, Week 8210 Derwent Publications Ltd., London, GB; Class A97, AN 82-18376E XP002058106 &amp; JP 57 016 192 A (KIZAI KK) see abstract</td>
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<td>A</td>
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Further documents are listed in the continuation of box C. Patient family members are listed in annex.

**Date of the actual completion of the international search**

9 March 1998

**Date of mailing of the international search report**

18/03/1998

**Name and mailing address of the ISA**

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Van Leeuwen, R
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<th>Publication date</th>
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