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"A PROCESS FOR THE PRODUCTION OF IMPROVED CORROSION RESISTANT
ZINC COATINGS ON STEEL SUBSTRATES BY ELECTRODEPOSITION".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rajiv Market,
New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XII of 1860).

The following specification describes the nature of this invention.

PRICES: TWO RUPEES
This is an invention by Balkunja Anantha Shenoi, and Mrs. Malathy Pushpavanam, Scientists of the Central Electrochemical Research Institute, Karaikudi -623006, Tamil Nadu, India, both Indian Nationals.

This invention relates to the Improvement in or relating to the electrodeposition of corrosion resistant zinc deposits from acid and neutral baths.

Hitherto zinc has been deposited from acid and neutral baths and a conversion coating is given to improve the post-treatment step by introducing certain additives in the plating bath itself.

To these ends the invention broadly consists in the development of a process for the electrodeposition of corrosion resistant zinc coatings from acid and neutral baths by addition of suitable addition agents in the plating bath itself. The bath compositions are as follows:

I. Zinc sulfate : 200-300 g/l
   Boric acid : 25-40 g/l
   Sodium chloride : 10-30 g/l
   Aluminium sulphate : 10-30 g/l
   Cobalt sulphate : 10-30 g/l
   Chromium sulphate : 0.5 - 2 g/l
   at 3-10 A/dm² at 30-40°C

II. Zinc chloride : 30-50 g/l
    Sodium gluconate : 100-150 g/l
Boric acid : 30-60 g/l
Potassium chloride : 100-150 g/l
Cobalt sulphate : 10-30 g/l
Chromic sulphate : 0.5 - 2 g/l
pH : 6 - 7
Current density : 3 - 5 A/dm²
Temperature : 30-35°C

The following are the examples given to illustrate the invention:

**EXAMPLE 1**

Zinc sulphate : 200 g/l
Aluminium sulphate : 15 g/l
Sodium chloride : 15 g/l
Boric acid : 30 g/l
Cobalt ion (as cobalt sulphate) : 10 g/l
pH : 3 - 4
Current density : 3 A/dm²
Temperature : 30-35°C

The deposits plated up to 15 micron thickness are 2 times more corrosion resistant than pure zinc deposits when tested in 5% sodium chloride salt spray test.

**EXAMPLE 2**

Zinc sulphate : 250 g/l
Aluminium sulphate : 15 g/l
Sodium chloride  :  15 g/l  
Boric acid        :  40 g/l  
Cobalt ion       :  10 g/l  
(as cobalt sulphate)  
Chromium ion     :  0.1 g/l  
(as chromic sulphate)  
PH                :  3 - 4  
Current density   :  1 - 4 A/dm²  

The 15 micron thick deposits are 2.5 - 3 times more corrosion resistant than pure zinc deposits when tested as before.

**EXAMPLE - 3**

Zinc chloride      :  20 g/l  
Sodium gluconate   :  120 g/l  
Boric acid         :  30 g/l  
Potassium chloride :  100 g/l  
Cobalt ion         :  10 g/l  
(as Cobalt sulphate)  
PH                 :  6 - 7  
Current density    :  3 A/dm²  

The 15 micron thickness deposits are 2 times more corrosion resistant than pure zinc deposits when tested as indicated above.

**EXAMPLE - 4**

Zinc chloride      :  50 g/l  
Sodium gluconate   :  120 g/l  
Boric acid         :  30 g/l
Potassium chloride 120 g/l
Cobalt ion 10 g/l
(as sulphate)
Chromium ion 0.1 g/l
(as sulphate)
pH 6 - 7
Current density 4 A/dm²

The 15 micron thick deposits are 2-3 times more corrosion resistant than pure zinc deposits when tested as before. The following are among the main advantages of this invention:

The addition of cobalt and/or chromium ions to the plating bath improves the corrosion resistance of the zinc plates and the deposits produced are 2-3 times more corrosion resistant than pure zinc deposits.

Dated this 31st day of July, 1979.

Sd/-

(I.M.S. MAMAK)
PATENTS OFFICER
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
COMPLETE SPECIFICATION

(Section—10)

"A PROCESS FOR THE PRODUCTION OF IMPROVED CORROSION RESISTANT ZINC COATINGS ON STEEL SUBSTRATES BY ELECTRODEPOSITION"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860)
This is an invention by BALKUNJE ANANTHA SHENOI, and Mrs. MALATHY
PUSHPAVANAM, Scientists of the Central Electrochemical Research
Institute, Karaikudi-623006, Tamilnadu, India, both Indian
nationals.

This invention relates to a process for the production of
improved corrosion resistant zinc coatings on steel substrates by
electrodeposition.

Hitherto zinc has been deposited on the steel substrates from
acid and neutral baths and is followed by the step of a
conversion coating to improve the corrosion resistance of the
coating.

The object of this invention is to improve the corrosion
resistance of zinc coatings on the steel substrates and eliminate
the costly additional step of conversion coating of the known
process by using a single step process by developing an improved
electrolytic bath for the purposes of electrolytic deposition of
zinc in an electrolytic cell known in the art. The addition of
cobalt and or chromium ions to the plating bath improves the
corrosion resistance of the zinc coatings which are 2-3 times
more corrosion resistant than that of pure normal zinc coatings.

The main finding of the invention is the development of a process
for the electrodeposition of corrosion resistant zinc coatings
from acid and neutral electrolytic baths by the addition
therein of cobalt/chromium ions.

The present invention accordingly consists of a process for the
production of improved corrosion resistant zinc coatings on steel substrates by electrodeposition in an aqueous bath which consists of zinc salts, boric acid, sodium gluconate and alkali metal salts in the presence of cobalt and/or chromium ions.

Accordingly this invention provides a process for the production of improved corrosion resistant zinc coatings on steel substrates by electrodeposition using an aqueous electrolytic bath containing acid/neutral zinc metal salts, which is characterised in that the electrodeposition is carried out in the said bath containing cobalt and/or chromium ions using an electroplating cell known per se.

According to a feature of the invention the electrolytic bath contains cobalt ions in the form of cobalt sulphate in an amount of 10 - 30 g/l of the electrolytic solution.

According to a further feature of the invention the electrolytic bath contains chromium ions in the form of chromic sulphate in an amount of 0.5 - 2 g/l of the electrolytic solution.

According to a further feature of the invention electrolytic bath consists of an aqueous solution of 200-300 g/l of zinc sulphate or 30-50 g/l of zinc chloride, 25-40 g/l of boric acid, 0-30 g/l of aluminium sulphate, 10-30 g/l of sodium chloride or 100-120 g/l of potassium chloride, 0-120 g/l of sodium gluconate and 0.5 - 2 g/l of chromic sulphate or 10-30 g/l of cobalt sulphate and wherein the electrodeposition reaction is carried out at current density of 3-10 A/dm², pH of 3-7 and a temperature of 30-40°C.
According to an additional feature of the invention the electrolytic bath used consists of an aqueous solution of 20 g/l of zinc chloride, 120 g/l of sodium gluconate, 30 g/l of boric acid, 100 g/l of potassium chloride and 10 g/l of cobalt ions as sulphate or 0.1 g/l of chromium ions as sulphates.

The bath compositions according to the invention are as follows:

**Acid bath:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc sulfate</td>
<td>200-300 g/l</td>
</tr>
<tr>
<td>Boric acid</td>
<td>25-40 g/l</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>10-30 g/l</td>
</tr>
<tr>
<td>Aluminium sulfate</td>
<td>10-30 g/l</td>
</tr>
<tr>
<td>Cobalt sulfate</td>
<td>10-30 g/l</td>
</tr>
<tr>
<td>Chromium sulfate</td>
<td>0.5-2 g/l</td>
</tr>
<tr>
<td>Current density</td>
<td>3-10 A/dm²</td>
</tr>
<tr>
<td>Temperature</td>
<td>30-40°C</td>
</tr>
<tr>
<td>pH</td>
<td>3-4</td>
</tr>
</tbody>
</table>

**Neutral bath:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc chloride</td>
<td>30-50 g/l</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>10-150 g/l</td>
</tr>
<tr>
<td>Boric acid</td>
<td>30-60 g/l</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>100-150 g/l</td>
</tr>
<tr>
<td>Cobalt sulfate</td>
<td>10-30 g/l</td>
</tr>
<tr>
<td>Chromic sulfate</td>
<td>0.5-2 g/l</td>
</tr>
<tr>
<td>pH</td>
<td>6-7</td>
</tr>
</tbody>
</table>
Current density ... 3-5 A/dm²
Temperature ... 30-40°C

The process of the invention is further illustrated by the following examples.

**EXAMPLE-1**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc sulfate</td>
<td>200 g/l</td>
</tr>
<tr>
<td>Aluminium sulfate</td>
<td>15 g/l</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>16 g/l</td>
</tr>
<tr>
<td>Boric acid</td>
<td>30 g/l</td>
</tr>
<tr>
<td>Cobalt sulfate</td>
<td>10 g/l</td>
</tr>
<tr>
<td>pH</td>
<td>3-4</td>
</tr>
<tr>
<td>Current density</td>
<td>3 A/dm²</td>
</tr>
<tr>
<td>Temperature</td>
<td>30-38°C</td>
</tr>
</tbody>
</table>

The deposits plated up to 15 micro meter thickness are 2 time more corrosion resistant than pure zinc deposits when tested in 5% sodium chloride salt spray test. The pure deposit withstood only 120 hrs. salt spray.

**EXAMPLE-2**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc sulfate</td>
<td>250 g/l</td>
</tr>
<tr>
<td>Aluminium sulfate</td>
<td>15 g/l</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>15 g/l</td>
</tr>
<tr>
<td>Boric acid</td>
<td>40 g/l</td>
</tr>
<tr>
<td>Cobalt sulfate</td>
<td>10 g/l</td>
</tr>
<tr>
<td>Chromic sulfate</td>
<td>0.1 g/l</td>
</tr>
</tbody>
</table>
pH \hspace{1cm} \ldots \hspace{1cm} 3-4

Current density \hspace{1cm} \ldots \hspace{1cm} 3 \text{ A/dm}^2

The 15 micro meter thick deposits are 2.5-3 times more corrosion resistant than pure zinc deposits when tested as before. The pure deposit withstood only 120 hrs. salt spray whereas the deposits obtained from the above bath withstood 300 hrs. salt spray.

**EXAMPLE-3**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc chloride</td>
<td>30 g/l</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>120 g/l</td>
</tr>
<tr>
<td>Boric acid</td>
<td>30 g/l</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>100 g/l</td>
</tr>
<tr>
<td>Cobalt sulfate</td>
<td>10 g/l</td>
</tr>
<tr>
<td>pH</td>
<td>6-7</td>
</tr>
<tr>
<td>Current density</td>
<td>3 A/dm$^2$</td>
</tr>
</tbody>
</table>

The 15 micro meter thick deposits are 2 times more corrosion resistant than pure zinc deposits. The pure deposit withstood only 120 hrs. salt spray whereas the deposit obtained from the above bath withstood 240 hours salt spray.

**EXAMPLE-4**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc chloride</td>
<td>50 g/l</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>120 g/l</td>
</tr>
<tr>
<td>Boric acid</td>
<td>30 g/l</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>120 g/l</td>
</tr>
<tr>
<td>Cobalt ion(as sulfate)</td>
<td>10 g/l</td>
</tr>
<tr>
<td>Chromium ion(as sulfate)</td>
<td>0.1 g/l</td>
</tr>
</tbody>
</table>
The 15 micro meter thick deposits are 2-3 times more corrosion resistant than pure zinc deposits when tested as before. The pure deposit withstood only 120 hours salt spray whereas the deposit obtained from the above bath withstood 300 hours salt spray.

More corrosion resistant zinc deposits can be obtained from acid and neutral zinc baths containing (a) zinc sulfate 200-300 g/l, boric acid 25-40 g/l, sodium chloride 10-30 g/l, aluminium sulfate 10-30 g/l, cobalt sulfate 10-30 g/l, chromic sulfate 0.5-2 g/l at 3-10 A/dm$^2$ with pH 3-4 and at 30-40°C (b) Zinc chloride 30-50 g/l, sodium chloride 100-150 g/l, boric acid 30-60 g/l, potassium chloride 100-150 g/l, cobalt sulfate 10-30 g/l, chromic sulfate 0.5 - 2 g/l, pH 6-7, current density 3-5 A/dm$^2$, temperature 30-35°C.

WE CLAIM:

1. A process for the production of improved corrosion resistant zinc coatings on steel substrates by electrodeposition using an aqueous electrolytic bath containing acid/neutral zinc metal salts characterised in that the electrodeposition is carried out in the said bath containing cobalt and/or chromium ions using an electroplating cell known parts.

2. Process as claimed in claim 1 wherein the electrolytic bath contains cobalt ions in the form of cobalt sulphate in an amount of 10-30 g/l of the electrolytic solution.
3. Process as claimed in claim 1 or 2 wherein the electrolytic bath contains chromium ions in the form of chromic sulphate in an amount of 0.5 - 2 g/1 of the electrolytic solution.

4. Process as claimed in any of the preceding claims wherein electrolytic bath consists of an aqueous solution of 200-300 g/1 of zinc sulphate or 30-50 g/1 of zinc chloride, 25-40 g/1 of boric acid, 0-30 g/1 of aluminium sulphate, 10-30 g/1 of sodium chloride or 100-120 g/1 of potassium chloride, 0-120 g/1 of sodium gluconate and 0.5-2 g/1 of chromic sulphate or 10-30 g/1 of cobalt sulphate and wherein the electrodeposition reaction is carried out at a current density of 3-10 A/dm², pH of 3-7 and a temperature of 30°-40°C.

5. Process as claimed in any of the preceding claims wherein the electrolytic bath used consists of an aqueous solution of 20 g/1 of zinc chloride, 120 g/1 of sodium gluconate, 30 g/1 of boric acid, 100 g/1 of cobalt ions as sulphate or 0.1 g/1 of chromium ions as sulphates.

6. A Process for the production of improved corrosion resistant coatings on steel substrates by electrodeposition substantially as herein described and illustrated with reference to the examples.

Dated this 15th day of September, 1980.

Sd/-

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