Paint ------------ Epoxy Type 60 Concentration----10 %  
Phosphotized Steel  

Plated Chromium  

Temperature------25°C  
Voltage---------60 v  

Electro-Deposition Time (Sec.)

Paint Coating Weight (mg/dm²)

0  10  20  30  40  50  60

0  2  4  6  8  10

Paint ------------ Epoxy Type
Concentration----10 %
Temperature------25°C
Voltage---------60 v

FIG 1
FIG. 2

Relation Between Zn Coating Weight and Corrosion Resistance

Chromium Coating Weight 5mg/dm²
Electro-Coating Conditions
Epoxy Type Paint
90v 25min.
Baking Condition
150°C 25min.
PROCESS FOR ELECTRODEPOSITION OF PAINT COATINGS ON ZINC-PLATED STEEL SHEET

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ABSTRACT OF THE DISCLOSURE

In a process for the electrodeposition of paint on zinc-plated steel, the improvement which comprises plating chromium on the zinc-plated surface of said steel and electrodepositing the paint on the chromium plating. By applying an intermediate chromium plating, contamination of the paint composition by zinc dissolving from the plating during paint electrodeposition is greatly diminished and excellent adhesion and rust prevention is obtained.

The present invention relates to a process for the electrodeposition of paint coatings on zinc-plated steel and products obtained therefrom. The zinc-plated steel products of the present invention have about 0.2 g/m² or more of zinc plated thereon. The coating weight throughout the specification and claims is shown as that on one side of the material. As is well known, the electrodeposition paint-coating process is a paint-coating process whereby coating material such as that of epoxy type, acrylic type, phenolic type, alkyd type, etc., dispersed or dissolved in an electro paint-coating solution, is electrodeposited on an article or product, e.g., zinc-plated steel. The article to be coated is placed in the solution or dispersion of the paint, using the article as anode with direct current passed thereto. This causes paint particles to adhere onto the article by electrophoresis.

Since zinc plated onto a steel surface effectively protects the steel from corrosion, zinc-plated steel products have been widely used for a long time. But steel products with only zinc plating are corroded in a relatively short period of time and adhesion of paint coatings thereto is not entirely satisfactory. Therefore, as a surface treatment for the zinc-plated steel products such chemical treatments as phosphate treatment and/or chromate treatment, etc., has been applied thereto. In case an organic coating is applied by the above-mentioned electrodeposition coating process to zinc-plated steel products with or without chemical treatment, the plated zinc and/or the chemically treated film are dissolved from the article when it is dipped into the paint-coating solution or dispersion and the article is electrically charged. This deteriorates the aqueous solution of the coating material. Also, this causes the coating material to be electrodeposited directly onto metallic zinc, which lowers the adhesion of the paint coating.

Thus the electrodeposition of a paint coating over zinc-plated steel products for corrosion resistance has been considered disadvantageous. In view of the above, it is an object of the present invention to provide a process for the electrodeposition of paint coatings on zinc-plated steel products wherein such coatings can be effectively applied and the adhesion of the paint coating onto the products is improved.

The above objects are attained by applying a chromium plating to zinc-plated steel products for a short period of time, prior to the electrodeposition of the paint coating. Zinc plating and chromium plating in the present invention can be by any of the methods conventionally known. The steel products should be washed with water after zinc plating and the chromium plating should preferably be done immediately thereafter. It is desirable to send the chromium plated steel sheet to the paint electrodeposition tank after water rinsing without drying the plated material. By doing so, the chromium-plated material can be paint coated by electrodeposition while it still preserves its chemically active state. This provides good adhesion of the paint coating and results in good corrosion resistance and workability.

The product obtained by the present invention has such advantages that red rusting is satisfactorily prevented because even when the coated film of paint is damaged the steel surface is protected by the zinc existing as underlying film.

The present invention shall be described referring to the attached drawings.

FIG. 1 is a diagram showing the relationship between the electrodeposition time and the thickness of electrodeposited paint coating film when the electrodeposition coating is given to various materials. FIG. 2 is a diagram showing the relationship between the coating weight and corrosion resistance of zinc-plated steel sheet with electrodeposition paint coating.

Table 1 shows the amount of zinc dissolved from the zinc plating into the aqueous electrodeposition paint solution from steel which had been zinc plated and then chromated, and from steel which had been zinc plated and then chemically treated.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Amount of zinc dissolved (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc only</td>
<td>0.058</td>
</tr>
<tr>
<td>Zinc + Cr</td>
<td>0.113</td>
</tr>
</tbody>
</table>

Conditions for chromate treatment:
- Sodium dichromate—80 g/l.
- Sulphuric acid—0.3 g/l.
- Nitric acid—1.0 g/l.
- Temperature 50°—50° C.
- Time—2 seconds.

Conditions for phosphate treatment:
- Bonderite #37 (commercial name, available from Hooker Chemical Corp.) is used.
- Free acid—1.1
- Total acidity—15.4
- Acid ratio—14
- Concentration—35 g/l.
- Temperature—50° C.
- Time—2 minutes.
Conditions for electrodeposition coating:

Epoxy type electrodeposition coating material is used.

Voltage—9 v.
Time—3 minutes.
Coating temperature—35°C.
Conditions for zinc plating:
Zinc sulphate—250 g/l.
Sulphuric acid—1.8 g/l.
Aluminium sulphate—15 g/l.
Temperature—40°C.
Current density—30 A./dm².

The conditions for electrodeposition coating when electrodeposition coating is given to various materials for a short period of time. It shows much more effectively the electrodeposition coating film is obtained on plated chromium used in the present invention for surface treatment of zinc-plated steel sheet compared to other materials.

Next, Table 2 shows the adhesion properties of electrodeposition paint coating film of a zinc-plated steel sheet, the same sheet with chemical treatment applied thereon, and the zinc-plated steel sheet with electrochromium plating applied thereon.

### Table 2: Paint Adhesion Tests

<table>
<thead>
<tr>
<th>Material</th>
<th>Scratch Test</th>
<th>Erichsen Cup Value (mm.)</th>
<th>Impact Test (weight-height)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro galvanized steel sheet (zinc coating weight, 18 g/m²)</td>
<td>X</td>
<td>3.1</td>
<td>X</td>
</tr>
<tr>
<td>Electro galvanized steel sheet with chrome treatment applied thereon (zinc coating weight, same as above)</td>
<td>X</td>
<td>7.8</td>
<td>0</td>
</tr>
<tr>
<td>Electro galvanized steel sheet with phosphoric treatment applied thereon (zinc coating weight, same as above)</td>
<td>X</td>
<td>7.9</td>
<td>0</td>
</tr>
</tbody>
</table>

The tests were conducted at 37°C. for one week. The test pieces were drawn 8 mm. deep with an Erichsen tester and peeling off of the organic coating was observed. In the table the marks indicate as follows:
O = No defects in the coating.
X = Coating partly damaged.
Δ = Coating completely damaged.
Thickness of steel sheet: 0.8 mm.

The conditions for zinc plating, chromium plating, phosphoric treatment, and electrodeposition coating are same as those in Table 1.

In impact test, DuPont type tester with a weight of 1 kg. and a punch die with 3/4” diameter was used.

The above table shows that the amount of chromium plated, about 1.5 mg/m² or more is desirable. The maximum amount of chromium plated should be about 7 mg/m² from a standpoint of workability. More than 7 mg/m² of chromium coating when it is bent or drawn. As to the amount of zinc plated, it may be such amount as ordinarily used in conventional zinc-plated steel sheet, that is about 9 g/m² to 60 g/m² on electro-
galvanized steel sheet and about 30 g./m.² to 230 g./m.² on galvanized steel sheet (both one side), but it can be such amount as far less than those, that is, about 0.2 g./m.². The zinc plated in an amount smaller than that will result in inferior corrosion resistance, as shown in FIG. 2.

FIG. 2 shows red rust formation time on the cross-cut portions of steel sheets having different amount of zinc plated thereon, with a certain amount of chromium plating and electrodeposition paint coating thereon, which were cross-cut on the surface and was salt water sprayed.

FIG. 2 indicates that when the amount of zinc plated is more than about 0.2 g./m.², the corrosion resistance after electrodeposition coating is good.

It was confirmed by electrode potential measurement in 0.1 N-H₂SO₄ that when the amount of zinc plated is less than 0.2 g./m.², zinc potential was not shown.

That is, the steel sheet, which has more than 0.2 g./m.² of zinc plated thereonto and 1.5 to 7.0 mg./dm.² of chromium plated thereover and then is subjected to electrodeposition coating, has excellent paint coating adhesion, corrosion resistance and workability.

What is claimed is:

1. In a process for the electrodeposition of paint on zinc-plated steel, the improvement which comprises plating chromium on the zinc-plated surface of said steel and electrodepositing the paint on the chromium plating.

2. A process of claim 1 wherein the steel is rinsed with water after chromium plating and subjected to the electrodeposition of the paint while still wet from said rinsing.

3. A process of claim 1 wherein the amount of zinc plating is greater than about 0.2 g./m.² and the amount of chromium plated is about 1.5 mg./dm.² to 7.0 mg./dm.².

4. A process of claim 2 wherein the amount of zinc plating is greater than about 0.2 g./m.² and the amount of chromium plated is about 1.5 mg./dm.² to 7.0 mg./dm.².

5. A process of claim 1 wherein the amount of zinc plating is about 0.2 g./m.² and the amount of chromium plated is from about 1.5 mg./dm.² to 7 mg./dm.².

6. A process of claim 2 wherein the amount of zinc plating is 0.2 g./m.² to 9 g./m.² and the amount of chromium plated is from about 1.5 mg./dm.² to 7 mg./dm.².

7. A process of claim 2 wherein the paint coating is selected from epoxy, acrylic, phenolic or alkyd type coatings.

8. A steel article having an electrodeposited paint coating prepared by the process of claim 1.

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