FIG. 9
ACID ZINC-ELECTROPLATING PROCESS AND PRODUCT THEREOF

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ABSTRACT OF THE DISCLOSURE

A layer of zinc is formed on steel plates by electrolysis from an acid-zinc-electroplating bath containing 0.05 to 0.3 g./l. of Cr+6 ions. The plated steel is characterized by excellent corrosion resistance, and provides excellent adhesion to ordinary paints. In a second embodiment of this invention, the steel may have an initial plate of zinc in a thickness of at least 1 x 10^{-3} mm prior to said electrolysis treatment.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to an acid zinc-electroplating process for use on steel plates or the like, which gives plated zinc layers which have excellent corrosion resistance properties and which have surfaces suitably adapted for painting.

Description of the Prior Art

It is known that acid zinc-electroplating processes can be adapted to improve the corrosion resistance of steel plates or the like. The electroplating baths used for the plating of steel sheets usually contain therein as a basic agent containing zinc ions, electro-conductive salts, to improve the electrical conductivity of the bath, and a buffer agent to maintain the pH of the plating medium at a predetermined value. Since an electroplated layer or film, which is obtained from such a bath is usually pure zinc, the plated layer obtained is initially a uniform gray-white color. This layer, however, takes on the undesirable appearance of white rust in an extremely short period of time after the plated sheet is stored in an atmosphere with a high level of humidity. In addition, in instances in which the metal is a steel plate, the plates eventually develop rust. The time it takes for the initial appearance of rust on the steel plates in a salt spray test is proportional to the thickness of the plated layer, that is, it takes an additional 6 to 8 hours for rust to appear for each additional micron of the plated layer.

An additional disadvantage of conventional zinc-plating procedures is that the plated layer does not have a surface suitable for painting because of the poor adhesion of the paint to the surface of the layer. This results in peeling of the paint from the layer. The surface of the exposed layer must be further treated, such as by chromating or phosphating treatments to improve the corrosion resistance and to improve the ability of paint to adhere to the layer.

When a baked finish is desired on the electroplated layer, blisters will often develop in the baking process in the interface between the surface of the base metal and the electroplated layer. This results in critical defects in the metal. The blisters are believed to be caused by the presence of a very small amount of hydrogen formed during the electroplating process which becomes occluded or otherwise contained on the surface of the base metal.

A need, therefore, exists for an electroplating process which yields a zinc plated base metal which is not easily corroded and to which paint coating can be firmly adhered.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide an improved acid zinc-electroplating process.

Another object of the invention is to provide an improved acid zinc-electroplating process which yields a metal product having highly improved corrosion resistance and an improved bondability to paint coatings.

These and other objects of this invention as hereinafter will become readily apparent to one of ordinary skill in the art, is attained by providing, in a first embodiment of this invention, an acid zinc-electroplating process for use on steel plates or the like, which comprises the electrolysis of a metal sheet in an acid-zinc-electroplating bath containing 0.05 to 0.3 g./l. of Cr+6 ions.

In a second embodiment of this invention, an acid zinc-electroplating process is provided wherein zinc is plated in a thickness of 1 x 10^{-3} mm onto the surface of base metal and then said plated metal is further subjected to electrolysis in an acid-zinc-electroplating bath containing 0.05 to 0.3 g./l. of Cr+6 ions. The electroplated steel plates thus produced are characterized by excellent corrosion resistance and highly improved adhesive properties for paint films applied thereon.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein: FIG. 1 is an X-ray diffraction diagram of the plated layers produced by the process of this invention (1) and by conventional acid zinc-electroplating procedures (2); FIG. 2 shows infrared spectra of a layer (3) produced by the acid zinc-electroplating process of this invention, a layer (4) obtained from conventional acid zinc-electroplating procedures, and a layer (5) on a steel plate which has been subjected to an electrolytic chromating process; FIG. 3 is a plot obtained by an electron probe microanalyzer showing the chromium distribution throughout an electroplated layer produced by the process of this invention; FIG. 4 is a plot showing the relationship between the electrode potential and the current density for Zn-Cr electroplating a mild steel plate; FIG. 5 is a plot showing the relationship between the electrode potential and the current density for Zn-Cr electroplating a pure zinc layer 0.14 mm thick; FIG. 6a shows the development of blisters throughout the surface of a sample having both surfaces electroplated; FIG. 6b shows no development of blisters on the surface of a sample having one surface electroplated; FIG. 6c shows no development of blisters on the surface of a sample which has been subjected to the acid zinc-electroplating process of the present invention; FIG. 7 is a plot showing the relationship between electrode potential and the thickness of a plated zinc layer; FIG. 8 is a perspective view of a tester used in testing the present invention; FIG. 9 is a photograph showing the results of peeling tests conducted on plated metal sheets which have had patterns described on their surfaces with the describing tester of FIG. 8.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the process of the present invention, a small amount of Cr+6 ions is added to an acid zinc-electro-
plating bath. The amount of ions added is in the range of 0.05 to 0.3 g/l. If Cr\textsuperscript{6+} ions are present in concentrations of less than 0.05 g/l, no appreciable improvements are seen in the corrosion resistance of the plated steel plates. If Cr\textsuperscript{6+} ions are present in concentrations of greater than 0.3 g/l, the final appearance of the electroplated steel plates will be appreciably spoiled. The chromium ions can be added to the bath in the form of compounds of Cr\textsuperscript{6+} such as CrO\textsubscript{3}, K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} and/or (NH\textsubscript{4})\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}. The pH of the bath should preferably be adjusted to the range of 2.5 to 4.5. If the pH is less than 2.5, poor effects are noted because of the presence of Cr\textsuperscript{6+} ions, while if the pH is greater than 4.5, zinc hydroxide could precipitate from the bath.

The concentration of zinc ions in the electroplating bath is in the range of 30 to 150 g/l, preferably 40 to 110 g/l. Suitable zinc salts which are added to the electroplating bath include ZnSO\textsubscript{4}, H\textsubscript{2}O, ZnCl\textsubscript{2}, Zn(BF\textsubscript{4})\textsubscript{2}, Zn\textsubscript{3}P\textsubscript{2}O\textsubscript{7} and the like. The thickness of the zinc layer on the plated metal sheets obtained from the acid zinc-electroplating bath is ten microns or less.

The salt spray test reveals, according to the present invention, that the corrosion resistance of the plated layer on a steel plate is three times greater than a layer obtained by conventional processes which do not contain Cr\textsuperscript{6+} in the electroplating baths.

The reasons for the improved corrosion resistance of the layer obtained from the acid zinc-electroplating process of this invention are based on the following facts. The analysis of the chromium content in the plated layer obtained by the process of the present invention indicates that from 0.05 to 0.6% chromium is contained in the plated zinc layer depending on the electroplating conditions. An attempt to define the characteristics of the electroplated layers (i) X-ray diffraction tests of plated layers, revealing the condition of the co-deposits of chromium and zinc contained in the plated layers, (ii) infrared spectra of the plated layers and (iii) electron probe microanalyzer tests which analyze for chromium in the plated layer have been used. The X-ray diffraction tests (FIG. 1) show that the layer obtained by the process of the present invention presents a diffraction image (1) of metallic zinc, similar to the diffraction image (2) of the plated layer obtained from a conventional acid zinc-electroplating bath.

On the other hand, the infrared spectrum (3) (FIG. 2) of the plated layer produced by a bath containing Cr\textsuperscript{6+} ions has absorption bands in the neighborhood of 590 and 1130 cm\textsuperscript{-1}. These absorption bands are considered to correspond to the absorption bands at 610 and 1130 cm\textsuperscript{-1}, which are obtained from an infrared spectrum of the chromat film on a steel plate which has been subjected to electrolytic plating. It is felt that these absorption patterns suggest the existence of chromium hydride. Thus, it can be considered that in the process of zinc electroplating in the presence of Cr\textsuperscript{6+} ions, chromium co-deposits as chromium hydride simultaneously with the precipitation of zinc. Furthermore, it is considered that the deformation, and stretching vibration of OH are responsible for the absorption patterns at 1600 and 3200 cm\textsuperscript{-1}. However, the plated layer obtained from a conventional acid-zinc-electroplating bath indicates (4) that the stretching vibration of OH only is in the neighborhood of 3200 cm\textsuperscript{-1}.

The results of a chromium analysis of the cross section of a plated layer obtained from a bath of the present invention, as determined by an electron probe microanalyzer, are shown in FIG. 3. The spectrum indicates a uniform distribution of chromium depthwise in the plated layer (10) as compared to the spectrum of a base steel sheet (11). In other words, unlike the distribution obtained by the chemical treatment of the surface of a plated layer, chromium is distributed throughout the depth of the layer which results in increased corrosion resistance. Because of the uniform distribution of chromium on the surface of the plated layer, the "as-plated" condition of the layer obtained by the process of the present invention can be maintained without the formation of nickel-chromating, thus providing improved corrosion resistance for the zinc plated steel plate.

As can be seen from the foregoing description, electrolysis of a sheet of metal in an acid zinc-electroplating bath containing a specific amount of Cr\textsuperscript{6+} ions therein affords a plated electroplating bath containing essential improvements in corrosion resistance as compared with the plated layers obtained from conventional acid-zinc-electroplating baths.

In addition, studies have been conducted on the problems associated with the adhesion of paint films to the plated layers as will be described hereinafter. A basic problem exists in that when a finish is baked on a plated layer of a steel plate which has been obtained from an electrolysis bath, there appears blisters on the interface between the base metal and the plated layer from the thermal effects of baking. This gives a defective appearance to the plated surface of the metal sheet.

Further studies by the applicants have revealed, however, that the development of blisters can be attributed to the presence of a very small amount of hydrogen which has occluded or is contained on the base metal, such as a steel plate during electrolysis. In order to solve this problem it has been found that the formation of hydrogen, and hence the formation of blisters which would have appeared in a subsequent baking step, can be completely prevented by first electroplating a normal or pure layer of zinc of a specific thickness on the metal sheet prior to electrolysis in the acid zinc-electroplating bath containing Cr\textsuperscript{6+} ions. This is well substantiated by FIGS. 4, and 5, which show the potential (mv. vs. SCE)—current (a./dm\textsuperscript{2}) curves measured for an acid zinc-electroplating bath containing Cr\textsuperscript{6+} ions therein with regard to the instances where a mild steel sheet is plated and a zinc-plated mild steel sheet having a 0.1x thick plated layer is plated, respectively. As can be seen from FIG. 4, when a mild steel sheet is electroplated in an agitated acid-zinc-electroplating bath containing Cr\textsuperscript{6+} ions, hydrogen is evolved in the neighborhood of -1150 mv. vs. SCE (20) prior to the Zn-Cr deposition at -1200 mv. vs. SCE (21). On the other hand, when a mild steel sheet having an electroplated layer of pure or normal zinc 0.1x thick plated thereto is electroplated in an acid zinc-electroplating bath containing Cr\textsuperscript{6+} ions, co-deposition of Zn-Cr at -1200 mv. vs. SCE (30) takes place prior to the development of hydrogen at -1400 mv. vs. SCE (31) (FIG. 5).

In another set of experiments, three samples of a mild steel plate 0.8 mm. thick, which were identified as plates A, B, and C were prepared. Plate A was electroplated on both surfaces in an acid-zinc-electroplating bath containing Cr\textsuperscript{6+} ions therein to produce layers 10x thick. Plate B was electroplated on one of its surfaces to produce a layer 10x thick. Plate C was first plated with pure or normal zinc to produce a layer 0.1x thick followed by an electroplating step in the acid-zinc-electroplating bath containing Cr\textsuperscript{6+} ions therein to produce an additional layer 10x thick. The samples were then subjected to a boiling water immersion test. After 30 minutes immersion, blisters appeared throughout the surfaces of Plate A which had been electroplated on both of its surfaces in an acid-zinc-electroplating bath containing Cr\textsuperscript{6+} ions therein (FIG. 6a). However, only minute blisters appeared on the surface of Plate B which had been electroplated on one side (FIG. 6b). This suggests that in the case of Plate C, the hydrogen produced can escape through the surface of the steel plate which has not been electroplated. However, in the case of Plate A, where both sides had been electroplated, the hydrogen produced cannot find its way out to the surface of the steel plate, because of the presence of blocking surface layers. This results in the eventual formation of blisters.
On the other hand, in the case of a steel sheet which has been electroplated with pure or normal zinc prior to electroplating in an acid zinc-electroplating bath containing Cr⁺⁺ ions therein, despite the plating on both of its surfaces, no blisters developed on either of its surfaces (FIG. 6c). As can readily be appreciated from the foregoing test results, the blisters produced on the interface between the base metal and the plated layer during the baking step can be attributed to the presence of hydrogen which has evolved during the electrolysis and has occluded or is contained on the base metal. Thus, one of the most effective, preventive approaches to this problem is the electrolysis of a metal sheet in an acid zinc-electroplating bath containing Cr⁺⁺ ions therein, coupled with the preparatory step of plating the base metal with pure zinc. Furthermore, experiments have shown that the minimum thickness of the plated zinc layer necessary for preventing an outbreak of blisters is $1 \times 10^{-3} \mu$. This is well represented by FIG. 7, which is a plot of the potential of an electrode versus the thickness of a plated zinc layer in microns. The plot shows the change in the electrical potential from a base sheet (40) at a potential of $-720$ mv. vs. SCE to that of zinc plated sheet (41) at a potential of $-1020$ mv. vs. SCE with respect to the thickness of the plated zinc layer. When the thickness of the zinc layer exceeds about $1 \times 10^{-3} \mu$, the curve indicates that the potential is completely shifted to that of zinc. The development of hydrogen and hence the occlusion thereof is prevented during the electrolysis, thus indicating that it is necessary to maintain the thickness of the zinc layer greater than $1 \times 10^{-3} \mu$.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

Example 1 shows a conventional art process for electroplating a metal sheet. Examples 2-8 represent the first embodiment of the electroplating process of this invention. Examples 9-11 represent the second embodiment of the electroplating process of this invention.

**EXAMPLE 1**

A mild steel sheet was electroplated under the following conditions to achieve plated layers of a thickness of 4μ.

<table>
<thead>
<tr>
<th>Bath Composition:</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄·7H₂O -------- 300 g/l.</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ -------- 30 g/l.</td>
</tr>
<tr>
<td>NH₄Cl -------------- 0.15 g/l. (Cr⁺⁺: 0.08 g/l.).</td>
</tr>
</tbody>
</table>

**Electrolytic Conditions:**
- pH of Bath -------- 4.0
- Temperature of Bath -------- 50° C.
- Current density -------- 30 A/dm².
- Electroplating time -------- 28 sec. (corresponding to a layer 4μ thick).

The metal sheet was covered with a coating of paint similar to that of Example 1.

**EXAMPLE 4**

<table>
<thead>
<tr>
<th>Bath Composition:</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄·7H₂O -------- 350 g/l.</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ -------- 40 g/l.</td>
</tr>
<tr>
<td>Cr₂O₃ -------------- 0.36 g/l. (Cr⁺⁺: 0.13 g/l.).</td>
</tr>
</tbody>
</table>

**Electrolytic Conditions:**
- pH of Bath -------- 3.8
- Temperature of Bath -------- 50° C.
- Current density -------- 30 A/dm².
- Electroplating time -------- 28 sec. (corresponding to a layer 4μ thick).

The metal sheet was covered with a coating of paint similar to that of Example 1.
Bath Composition:
- ZnSO₄·7H₂O  450 g./l.
- (NH₄)₂SO₄  50 g./l.
- NH₄Cl  50 g./l.
- CrO₃  0.57 g./l. (Cr³⁺: 0.3 g./l.).

Electrolytic Conditions:
- pH of Bath  3.0.
- Temperature of Bath  65° C.
- Current density  30 a./dm.².
- Electroplating time  28 sec. (corresponding to a layer 4μ thick).

The metal sheet was covered with a coating of paint similar to that of Example 1.

EXAMPLE 9
A mild steel sheet was electroplated on its surfaces under the conditions below in which (i) pure zinc layers 1×10⁻³μ thick were first electroplated followed by (ii) a second electroplating step using an electroplating bath containing Cr³⁺ ions to give a layer 4μ thick.

(i) Pure or normal zinc electroplating conditions
Bath Composition:
- ZnSO₄·7H₂O  350 g./l.
- (NH₄)₂SO₄  30 g./l.

Electrolytic Conditions:
- pH of Bath  4.0.
- Temperature of Bath  50° C.
- Current density  30 a./dm.².

(ii) Conditions of acid zinc-electroplating bath containing Cr³⁺ ions
Bath Composition:
- ZnCl₂  250 g./l.
- NH₄Cl  100 g./l.
- K₂CrO₇  0.43 g./l. (Cr³⁺: 0.15 g./l.).

Electrolytic Conditions:
- pH of Bath  4.0.
- Temperature of Bath  60° C.
- Current density  20 a./dm.².

Table 1 gives the results from the corrosion resistance tests and the adhesion to paint film tests of the plated layers which have been obtained in Examples 1–11.

<table>
<thead>
<tr>
<th>Example</th>
<th>Appearance (ton color)</th>
<th>Adhesion of plated layer (close contact bending)</th>
<th>Corrosion resistance (salt spray test)</th>
<th>Paintability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Initial development (ZnO), hr.</td>
<td>Initial development (Fe₂O₃), hr.</td>
</tr>
<tr>
<td>1</td>
<td>Gray-white. No discrepancy...</td>
<td></td>
<td>&lt;1</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>1</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>1</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>1</td>
<td>80</td>
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<tr>
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<td>10</td>
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<td>3</td>
<td>95</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td>1</td>
<td>95</td>
</tr>
</tbody>
</table>

*Denotes the peeling of a plated layer from a mild steel plate.

It is apparent from the data in Table 1, that the corrosion resistance of the plated layers given in Examples 2 through 11 (layers plated according to the process of the present invention), is superior to that of Example 1 (layer plated according to the process of the prior art) and that the time required for the formation of rust test the layers formed by the process of the present invention is much longer than in the instance where a layer is formed by a process of the prior art.

Similarly, with regard to the adhesion of the layers to paint films, significant improvements have been noticed for the metals plated by the process of this invention. That is, the results of the helical pattern describing adhesion test and the cross-cut adhesion test material suggest that significant improvements over the prior art processes have been made in the adhesion of the plated layer to paint films (compare Example 1 with Examples 2 through 8). However, as is clear from Table 1, the best results are obtained when the second embodiment of the present invention is employed, wherein a pure zinc layer is applied to produce a layer on a metal sheet of a specific thickness, followed by electrolysis in an acid zinc-electroplating bath containing Cr³⁺ ions. This fact is well substantiated by the superior data obtained from Examples 9 to 11 in comparison to the data of Examples 1 through 8.

For a better understanding of the data shown in Table 1, the helical pattern describing adhesion test and the cross-cut adhesion test will be described in further detail. The helical pattern describing adhesion test is a test made by the tester shown in FIG. 8, wherein a needle 51 is mounted on the lower tip of the shaft 52 which extends vertically and is adapted to rotate. The needle is designed so that it may describe a helical pattern on a painted surface as shown in FIG. 9. Mounted on the top of the shaft 52 is a loading dish 53 on which is placed a weight 54 weighing 300±1 g. The diameter
of the helical pattern described is limited to 10 mm. while the length thereof is over 30 mm. After describing a helical pattern on the painted surface of a plated metal sheet, a piece of adhesive tape (such as Scotch tape) is placed on the sheet over the helical pattern. The tape is suddenly peeled from the sheet to observe how much of the paint film is removed from the metal sheet. FIG. 9 shows the inspection criteria.

The cross-cut adhesion test is a test in which the film of paint on a sample metal sheet is cut into a grid pattern with a blade such as a safety razor to a depth which reaches the electroplated surface of the metal sheet. The spacing between adjacent lines of the grid pattern is 1 mm., with eleven lines, longitudinal and lateral, being described so as to intersect each other at right angles. This provides 100 sections 1 mm.² in area. Then, a strip of adhesive tape is placed on the grid pattern and is suddenly peeled from the sample. The paintability or the adhesiveness of the paint coating on the plated layer is determined by the amount of paint removed. If all of the sections remain in tact, i.e., if no paint is removed from any of the 100 sections, then the layer is graded as "10" on a scale of "0" to "10." If paint is removed from all of the sections, the layer receives a grade of "0."

The data in the table for the first and second embodiments of the invention (Examples 2 to 11) indicate that the development of red rust in the plated steel sheets takes about three times longer to develop over the plated steel sheets of the prior art processes.

The paintability test in the table indicates that the best results are achieved when metal sheets are plated by the process of the second embodiment (Examples 9 to 11) when compared to the data of Examples 1 to 8.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

What is claimed as new and intended to be covered by Letters Patent is:

1. A process for improving the corrosion resistance and paintability of steel plate which comprises electroplating a pure zinc layer of at least 1 x 10⁻³ µ onto said steel plate and then subjecting said zinc-coated steel plate to electrolysis as cathode in an aqueous acidic zinc electroplating bath containing 0.03 to 0.3 g/l. Cr⁺⁺ therein to deposit an additional layer of zinc thereon.

2. The product of the process of claim 1.

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<th>Inventor</th>
<th>Number</th>
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<th>Inventor</th>
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<td>5/1969</td>
<td>Germany</td>
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GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

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