Statistical study of the chromating of electrodeposited zinc.

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ABSTRACT

The yellow chromating of zinc was examined systematically with the aid of statistically planned experiments. In the study the influence of various concentrations of Chrome(VI), Chrome(III), Iron(III) and Zinc(II) was revealed. The various factors were tested in relation to their influence on the color of the chromate deposits and the total amount of chrome deposited. Furthermore the corrosion resistance was measured by means of a newly developed method called corrosion measured by titration (CMT). The results of corrosion tests in neutral salt spray will be presented at the conference.

1. INTRODUCTION.

Pure zinc is an non-ignoble metal which is easily attacked by oxygen. In the presence of humid surroundings, the deposits will have a dull and unattractive appearance.

To prevent tarnishing and to preserve a bright and constant appearance, it is common practice to post-treat electrodeposited, bright zinc coatings.

The most widely used post-treatment process is chromating. The main reasons for the popularity of these processes are their simplicity of operation, the possibility of obtaining high corrosion resistance and the possibility of obtaining various colours (blue, yellow, black, olive drab among others).

In looking for high corrosion resistance in neutral salt spray test, the best results will be achieved with a yellow or olive drab chromate depo- sit. For non-military purposes the yellow chromate coating is the most commonly used.

The chemistry of yellow chromating electrolytes is quite simple and it is possible to obtain high corrosion resistance in electrolytes based on chromic acid and small additions of, for example, sodium chloride (if pH is adjusted with HCl).

In production, build-up of zinc and chromium(III) in the electrolyte can be observed. Furthermore if parts are dropped into the electrolyte a buildup of the metals from these parts can be observed as well.

Due to the changes in the constituents of the chromating solution changes in the colour, the brightness and/or the corrosion resistance of the deposit can be observed.

As all these characteristics are important parts of the quality of the products, it is important to be able to
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make corrections for changes in the electrolyte.

2. FUNDAMENTALS

Chromate coatings are produced from chromic acid or chromate solutions containing additives, most often inorganic or organic acids, exerting an activating action.

When zinc is submerged in the solution it will be oxidated by the acid and dissolve. Oxidation of zinc is connected to a reduction of $H^+$ and an evolution of $H_2$. The hydrogen reduces a certain amount of hexavalent chromium to the trivalent state. The reduction of $H^+$ results in a pH increase at the metal solution interface to a value at which trivalent chromium precipitates in the form of gelatinous chromium hydroxide. The structure of these amorphous chromium polymers has been studied by several authors [1], [2].

During the formation of the chromium(III) hydroxide, hexavalent chromium will be occluded in the gel. According to [2] the higher corrosion resistance obtained by yellow chromating compared to blue chromating is caused by the co-deposition of hexavalent chromium in the yellow chromate coatings. When the yellow chromate is damaged, the hexavalent chromium is reduced to trivalent chromium which form a new coating.

Iron in the solution will be oxidated from Iron(II) to Iron(III) followed by a reduction of hexavalent chromium to trivalent chromium. It has been shown that it is not the trivalent chromium in the solution which precipitates at the metal-solution interface.

In production the aging of chromate solutions is well known, but the effect of various contaminations is not clear. In the following, the influence of various constituents in a yellow chromating solution (chloride based) is examined.

3. THE EXPERIMENTAL PLAN

Because several factors influence the chromating process, it was necessary to focus on a limited part. A decision to examine the effect of variations in $CrO_3$, $CrCl_3$, $Zn(II)$ (added as $ZnCl_2$) and $Fe(III)$ (added as $FeCl_3$) was made.

To be able to evaluate the various results on a statistically "correct" foundation, the study was carried out using statistically planned experiments. For the sake of simplicity, a Taguchi orthogonal array was used. It was decided to evaluate each of the three parameters on two levels.

The levels of the parameters are shown in Table I.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Level 1</th>
<th>Level 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III) (g/l)</td>
<td>0</td>
<td>0,5</td>
</tr>
<tr>
<td>Zn(II) (g/l)</td>
<td>5,0</td>
<td>15,0</td>
</tr>
<tr>
<td>Cr(III) (g/l)</td>
<td>0,5</td>
<td>3,0</td>
</tr>
<tr>
<td>Cr(VI) (g/l)</td>
<td>5,0</td>
<td>10,0</td>
</tr>
</tbody>
</table>

Table I. Levels for the parameters

To avoid problems with unknown interaction effects, it was decided to include all two-factor interaction effects in the experimental plan. To include all parameters and their interactions it was necessary to use
a standard L₈ orthogonal array as shown in Table II.

<table>
<thead>
<tr>
<th>L₈</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
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<tbody>
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<td>2</td>
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<td>2</td>
<td>2</td>
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<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
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<td>1</td>
</tr>
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<td>2</td>
<td>1</td>
<td>2</td>
</tr>
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<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table II. An L₈ orthogonal array.

Because of the uncertainty of the interactions it was possible only to reduce the number of experiments from 16 (all combinations) to 8.

The parameters and their interactions were placed according to Table III. This resulted in the final experimental plan shown in Table IV.

<p>| Experimental plan |
|-------------------|----------------|</p>
<table>
<thead>
<tr>
<th>nr</th>
<th>Cr(VI)</th>
<th>Cr(III)</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0,5</td>
<td>0</td>
<td>5,0</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0,5</td>
<td>0,5</td>
<td>15,0</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>4,0</td>
<td>0</td>
<td>15,0</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>4,0</td>
<td>0,5</td>
<td>5,0</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0,5</td>
<td>0</td>
<td>16,0</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0,5</td>
<td>0,5</td>
<td>6,0</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>4,0</td>
<td>0</td>
<td>6,0</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>4,0</td>
<td>0,5</td>
<td>16,0</td>
</tr>
</tbody>
</table>

Table IV. Experimental plan.

<table>
<thead>
<tr>
<th>Electrodeposition of zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc concentration : 15 g/l</td>
</tr>
<tr>
<td>NaCN conc. : 35 g/l</td>
</tr>
<tr>
<td>NaOH conc : 110 g/l</td>
</tr>
<tr>
<td>CD : 2,5 A/dm²</td>
</tr>
<tr>
<td>Plating time : 40 min</td>
</tr>
<tr>
<td>The chromating process</td>
</tr>
<tr>
<td>HNO₃-dlp : 1 ml/l, 10 sek</td>
</tr>
<tr>
<td>Chromating time : 20s+20s</td>
</tr>
<tr>
<td>pH : 2,0</td>
</tr>
<tr>
<td>Temperature : 25°C</td>
</tr>
</tbody>
</table>

Table V. Experiment conditions
4. THE EXPERIMENTS

In each experiment the following was measured:
- The brightness of the chromate coated zinc.
- The colour of the chromate coating.
- The corrosion resistance measured by titration (CMT).
- Neutral salt spray (ASTM B117).

Since several factors may influence the chromating process, only the four parameters: CrO₃, Cr(III), Zn(II) and Fe(III) were varied, all other variables were kept constant.

Two kinds of test specimens were plated for each experiment. For the CMT test a special cylinder-shaped test specimen was plated and chromated according to the procedure in Table V.

Corrosion testing by CMT was carried out in a pH-stat. During corrosion of zinc the following reactions will take place:

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]  \hspace{1cm} (1)

And

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (2)

or

\[ O_2 + 4H^+ + 4e^- \rightarrow 2 H_2O \]  \hspace{1cm} (3)

The corrosion of zinc is connected to a consumption of H⁺. If pH is kept constant the corrosion rate can be measured as the rate of titration in a pH-stat [3].

The CMT measurements were carried out at pH 5.0 and the pH was kept constant in a pH-stat using 0.001M HCl for titration.

For measurement of brightness, color, amount of chromium in the chromate coating, steel sheets were plated in a cyanide zinc electrolyte and chromated according to Table V. Two sheets were produced in each experiment.

The brightness was measured using a Shimatsu 160 UV spectrophotometer at a wavelength of 600 nm.

The colour was measured using an artificial scale of yellow colors from 1 to 10. 1 is equivalent to 0005-Y10R (NCS: Neutral color system) and 10 is equivalent to 1050-Y30R (NCS).

5. RESULTS

Table VI Measurements

<table>
<thead>
<tr>
<th>Experiment</th>
<th>CO</th>
<th>BR</th>
<th>CMT</th>
<th>μA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>3</td>
<td>1.23</td>
<td>12.48</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td></td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>2</td>
<td>1.33</td>
<td>5.467</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td>8.178</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>1.5</td>
<td>1.26</td>
<td>14.51</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td></td>
<td>8.828</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>5</td>
<td>1.13</td>
<td>14.80</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td></td>
<td>8.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>1</td>
<td>1.49</td>
<td>13.76</td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td></td>
<td>13.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>7</td>
<td>1.13</td>
<td>6.727</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td></td>
<td>5.080</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7a</td>
<td>5</td>
<td>1.41</td>
<td>13.76</td>
<td></td>
</tr>
<tr>
<td>7b</td>
<td></td>
<td>19.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>7</td>
<td>1.23</td>
<td>9.535</td>
<td></td>
</tr>
<tr>
<td>8b</td>
<td></td>
<td>14.45</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CO: Colour of the chromate coating
BR: Brightness = Log reflection
CMT: Corrosion measured by titration.
Fig 1 Colour of chromate coating

Fig 2 Brightness (log T)
Fig 3. Signal to noise ratio brightness

Fig 4. CMT measurements
The colour of the chromate coating.

In Table VI large variations in colour are observed. Furthermore, on the individual steel sheets large variations in colour were observed. The colour is usually more intense at the edges of the steel strips. At a colour character of 1.5, the middle of the steel sheet had a colour looking like a blue chromate coating.

From an ANOVA analysis it is observed that the concentration of chromic acid, Fe(III), and Zn(II) influence the colour of the chromate coating (21.44%, 33.26% and 21.44% respectively).

In Figure 1 it may be observed that:
- Cr(III) does not influence the colour of the chromate coating significantly.
- Between chromic acid and Fe(III) concentration a minor interaction effect can be observed. None of the other interaction effects seem to be important to the colour of the chromate coating.

The most intense yellow colour is achieved at low zinc concentration (5 g/l), high chromic acid concentration (10 g/l) and at a high iron(III) concentration (0.5 g/l).

Brightness of the coating.

Brightness is measured as reflection. The values listed in Table VII are mean values of 8 measurements on different parts of the steel sheets. The brightness measured in this manner describes the polishing capability of the chromate solution.

According to an ANOVA analysis of the brightness measurements, the brightness is controlled by the iron(III) concentration (21.23%) and interaction between the iron(III) and the chromic acid concentration (24.88%).

In Figure 2 it appears that a high iron(III) concentration combined with a high chromic acid concentration gives a dull deposit. On the other hand at a low chromic acid concentrations the variations in iron(III) concentrations seem to have no significant effect.

The zinc concentration has a small influence on the brightness (10.18%) but the chrom (III) concentration does not have a significant effect.

CMT measurements.

An ANOVA analysis of the CMT results shows a large uncertainty of 54.5%. This is caused by some effect(s) which cannot be related to any of the parameters in the experiments.

In Figure 4 it is observed that addition of 0.5 g/l iron(III) increases the corrosion resistance. Furthermore an interaction effect between iron(III) and chrome(III) can be observed. Increased concentration of chrome(III) reduces the corrosion resistance.

The variations in chromic acid and zinc(II) concentrations do not have any significant effects.

6. DISCUSSION

The colour of the chromate coating

The variations in colour was primarily controlled by the chromic acid, the iron(III) and the zinc concent-
The iron(III) affects the brightness as well as the corrosion resistance. As iron(III) will oxidate zinc without any pH change at the metal-solution interface, it is likely that the effect of iron(III) can be explained by an etching effect. The etching of the zinc deposit gives a more porous deposit which can be attacked more easily by the chromate.

When testing for a relation between the colour of the chromate coating and the CMT measurements no significant relation was found. An intense yellow colour does not necessarily result in a high corrosion resistance.

The brightness of the coating

If a relation between brightness and corrosion resistance is tested it is observed that more dull deposits have a higher corrosion resistance. Due to the large uncertainty on the CMT-data it is not possible to identify the relationship between brightness and corrosion resistance at a highly significant level.

The CMT measurements.

Corrosion rate of electrodeposited zinc (from a cyanide electrolyte), non-chromated, has been measured to about 50-60μA/cm² (CMT measurement). All of the chromate coated test-speciments showed corrosion rates below 20μA/cm².

It is interesting to notice that a concentration of 0.5 g/l of iron(III) has a beneficial influence on the corrosion resistance of the chromate coating. It must be emphasized that the effects observed in the experiments can be dependent on the fixed process parameters (Chromating time, pH etc).

It is possible that changes in pH of the chromate solution or the process time will alter the relative size of the different effects.

A relation between neutral salt spray test and CMT will be presented at the conference.

7. CONCLUSION.

In the study the effects of changes in a yellow chromating solution has been evaluated.

Addition of iron(III) affects the colour of the chromate coating, the brightness of the coating and the corrosion resistance. It is noticed that iron(III) interacts with chromic acid concentration when speaking of the colour and the brightness of the coatings.

Addition of zinc(II) between 5g/l and 25 g/l has a little effect. Zinc primarily influences the appearance of the coating.

Chromium(III) additions between 0.5 g/l and 3.0 g/l have little effect. Increased concentrations of chromium(III) seem to reduce the corrosion resistance in CMT.

Variations in chromic acid concentration between 5 g/l and 10 g/l influence the colour of the chromate coating and the brightness. Due to noise in the CMT measurements, it was not possible to identify a significant effects of the variation in chromic acid concentration.
9. DEFINITIONS

CA: Chromic acid
FE: Fe(III)
CR: Chromium(III)
CO: Colour
BR: Brightness
CMT: Corrosion measured by titration
ANOVA: Analysis of variance

10 LIST OF REFERENCES.

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