PROCESS OF PRODUCING DYED CHROMATE SURFACES ON ZINC AND CADMIUM

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Claims. (Cl. 148—6.1)

The present invention relates to a process for providing a dyed corrosion resistant surface on zinc and cadmium. Zinc and cadmium are commonly rendered corrosion resistant by applying chromate conversion coatings to their surfaces. These coatings are formed by immersing the piece in a chromic acid solution. The resultant conversion coatings are usually clear, yellow tinted varying to a deep olive drab, or black. It is often desirable to obtain more decorative colors. The known techniques for coloring these coatings have been extremely limited. I have now discovered an economical and widely applicable method of dyeing such coatings to desired colors. It is an object of this invention to provide a process for dyeing conversion coatings on zinc and cadmium.

It is still another object of this invention to provide a process for producing a colored surface on zinc and cadmium.

My invention contemplates immersing zinc or cadmium in a chromic acid bath, of the type used to obtain conversion coatings, until an effective and reasonably thick chromate coating is built up. The piece is then removed, rinsed, and while wet, immersed in a leaching solution for a few seconds to as many as two or three minutes. Following the leaching treatment, the piece is removed, rinsed, and inserted in a dye solution until the desired color is obtained.

The initial conversion coating is applied by immersing the metal in a chromic acid solution containing 3 to 150 g./l. (grams per liter) of chromic acid (CrO₃); sulfate ions to give a CrO₃/SO₄ ratio from 3:1 to about 15:1; the nitrate ions to give a CrO₃/NO₃ ratio from about 1:1 to about 12:1. These components may be added as salts of sodium or potassium as well as in the form of acids. They should be added in acid form sufficient to give a pH of less than about 2 and preferably less than 1.0. Additional materials such as acetic acid or boric acid are often used in baths of this type. Treatment in this chromating solution is usually from about 10 to 30 seconds at room temperature. The type (color) of the conversion coating will affect the depth of color obtained. An iridescent yellow film, which is usually thicker than a clear coating, gives a dyed article with a deeper color than would be obtained from an initially clear coating.

The leaching treatment which immediately follows the chromating treatment is carried out in an aqueous alkaline solution prepared from anions such as hydroxide, carbonate, phosphate, silicate, etc. These solutions preferably contain from about 2 to about 40 g./l. of the alkaline chemical. The temperatures vary from room temperature to almost the boiling point of the solution, preferably between about 20° C. to 60° C. The time of leaching varies from about a few seconds to about two or three minutes. A preferred period is from ten to thirty seconds at room temperature. The choice of the particular leaching condition utilized is dependent upon the conversion coating first placed on the piece, and the subsequent dye used and color (shade) desired. Longer immersion in the leach solution and higher temperatures generally result in a greater amount of leaching which on subsequent dyeing results in a deeper color for given conditions.

After removal from the leach solution, the piece is rinsed and then immersed into a dye solution. A large number of dyes may be used, dependent upon the color desired. The particular dye solution utilized and the conditions, i.e., temperature, pH, etc., existing in the bath at the time of the dye application vary with the particular dye utilized, the type and condition of the conversion coating being dyed, and the color desired. The most effective dye concentration depends on the particular dye utilized. From about one-quarter to five grams per liter are satisfactory for most dyes, although other concentrations are also operative. Increasing the concentration usually increases the rate of absorption so that a specific depth of color is obtained in a shorter time. Increasing the time of immersion usually increases the depth of color desired. Times from five seconds to five minutes have been used; preferably about 30 to 90 seconds. The temperatures are not critical. They may range from room temperature (as low as 15° C.) to about 70° C. Higher temperatures increase the rate of dye absorption so that deeper colors are usually obtained in a shorter time. The pH of the dye solution will vary according to the particular dye utilized. A buffered solution may be useful in some cases where either alkaline or acid solutions are dragged into the dye solution.

Suitable leaching solutions have been prepared from potassium hydroxide, sodium phosphate, sodium silicate, sodium carbonate, potassium carbonate, sodium hydroxide; of these sodium hydroxide and sodium carbonate are preferred. It is also possible to leach the conversion coating in a water solution at temperatures in excess of about 70° C. Although this procedure may be used to produce light colors, the use of alkaline salts is preferred since more absorption of dye occurs to yield deeper colors.

For purposes of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given: Samples of zinc and cadmium surfaces were chromated in a solution containing 65 g./l. of chromic acid, 8 g./l. of sulfuric acid, 3.5 g./l. of nitric acid, and 13 g./l. of acetic acid. Treatment in this solution was from 10 to 30 seconds, usually at room temperature. The pieces were then water-rinsed,
leached, water-rinsed and dyed. The conditions for leaching and dyeing are given in the following table:

### Table 1

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Leach Chemical</th>
<th>Conc., g/l</th>
<th>Temp., °C</th>
<th>Time, Sec.</th>
<th>Dye Trade Name</th>
<th>Source</th>
<th>Chemical Description</th>
<th>pH</th>
<th>Conc., g/l</th>
<th>Temp., °C</th>
<th>Time, Sec.</th>
<th>Color Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH</td>
<td>7</td>
<td>32</td>
<td>20</td>
<td>Algokit Red 8. Clayton Yellow.</td>
<td>Hartman-Ledden Co.</td>
<td>Acid anthraquinone dye</td>
<td>8.7</td>
<td>1.0</td>
<td>49</td>
<td>45</td>
<td>Pink</td>
</tr>
<tr>
<td>2</td>
<td>KOH</td>
<td>15</td>
<td>21</td>
<td>30</td>
<td>do</td>
<td>Clayton Yellow.</td>
<td>Also called Thiozole Yellow. A diazonium dye</td>
<td>5.7</td>
<td>0.5</td>
<td>27</td>
<td>60</td>
<td>Greenish Yellow</td>
</tr>
<tr>
<td>3</td>
<td>NaPO₄·12H₂O...</td>
<td>23</td>
<td>49</td>
<td>16</td>
<td>do</td>
<td>Alizarin Yellow</td>
<td>An azoalkyl-sulfonic dye</td>
<td>7.6</td>
<td>0.5</td>
<td>21</td>
<td>60</td>
<td>Golden Yellow</td>
</tr>
<tr>
<td>4</td>
<td>Na₂SiO₃</td>
<td>23</td>
<td>35</td>
<td>30</td>
<td>do</td>
<td>Potlver Blue.</td>
<td>A class dye</td>
<td>7.7</td>
<td>0.25</td>
<td>21</td>
<td>60</td>
<td>Dark Blue</td>
</tr>
<tr>
<td>5</td>
<td>Na₂CO₃</td>
<td>29</td>
<td>90</td>
<td>25</td>
<td>do</td>
<td>Pontamine Black E.</td>
<td>E.I. du Pont de Nemours.</td>
<td>9.3</td>
<td>0.25</td>
<td>21</td>
<td>60</td>
<td>Blue</td>
</tr>
<tr>
<td>6</td>
<td>Hot Water</td>
<td>71</td>
<td>30</td>
<td>30</td>
<td>do</td>
<td>Pontamine Black F.</td>
<td>An acid coal tar dye</td>
<td>7.0</td>
<td>0.5</td>
<td>21</td>
<td>60</td>
<td>Brown</td>
</tr>
</tbody>
</table>

The surface coated is zinc or cadmium. This includes clad metal, plated surfaces, and galvanized surfaces.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

I claim:

1. A process for preparing dyed chromate conversion coatings comprising immersing an object surface with a metal selected from the class consisting of zinc and cadmium in a chromating solution containing between 3 and 150 g/l of chromic acid to form a chromate conversion coating, withdrawing and rinsing said metal, then immersing said metal in a leach solution as selected from the class consisting of water at a temperature in excess of 70° C., and aqueous alkaline solutions, withdrawing and rinsing said metal, and then immersing said metal in a dye solution until the desired color is obtained.

2. The process of claim 1 in which the surface metal is zinc.

3. The process of claim 1 in which the surface metal is cadmium.

4. The process of claim 1 in which the chromating solution contains between 65 g/l and 150 g/l of chromic acid.

5. A process for preparing dyed chromate conversion coatings comprising immersing a metal selected from the class consisting of zinc and cadmium between 10 and 30 seconds in a chromating solution containing between 3 and 150 g/l of chromic acid to form a chromate conversion coating, withdrawing and rinsing said metal, then immersing said metal between 10 and 30 seconds in an aqueous alkaline leach solution at a temperature between 20° C. and 60° C., and then immersing said metal between 30 and 90 seconds in a dye solution at a temperature between 20° C. and 50° C. until the desired color is obtained.

6. The process of claim 5 in which the metal is zinc.

7. The process of claim 5 in which the metal is cadmium.

8. The process of claim 5 in which the chromating solution contains about 65 g/l of chromic acid.

References Cited in the file of this patent

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