

# Chromate conversion coating and alternatives as corrosion-resistant treatments for metal parts

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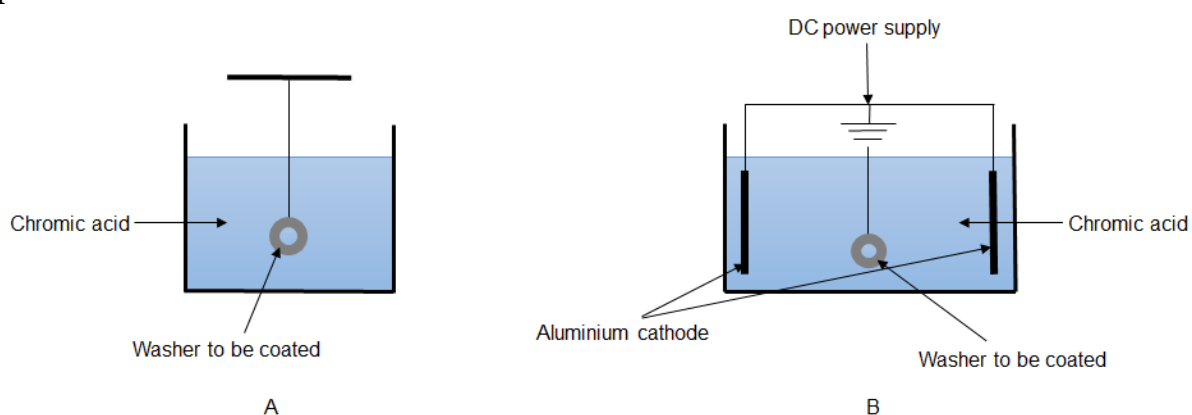
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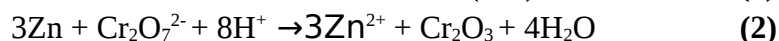
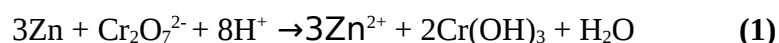
## 1.0 Introduction

Hexavalent chromium ( $\text{Cr}^{6+}$ ) conversion coating (CCC) serves as a corrosion inhibitor in metals, such as zinc and its alloys, magnesium and its alloys, aluminium and cadmium. The corrosion inhibition is attributed to an inert barrier created on the metal surface.<sup>1</sup> The conversion coating process involves immersion of a metal part in chromic acid, which is elaborated later in the report. Chromate conversion coating is distinct from chromic acid anodizing (see Figure 1), because anodizing involves an electrochemical method whereby the metal surface is converted into an oxide. The anodizing coating provides a harder and thicker coating as well as better corrosion protection on zinc surfaces as compared to the chromate conversion coatings, but issues such as cost, complexity, and aerosolization of  $\text{Cr}^{6+}$  are problematic.<sup>2</sup>



**Figure 1. A:** chromate conversion coating set-up. **B:** chromic acid anodizing set-up.

A chromate conversion coating is formed when the metal surface oxidizes in the chromic acid bath and hexavalent chromium ( $\text{Cr}^{6+}$ ) is reduced to the trivalent state ( $\text{Cr}^{3+}$ ). The reactions below provide possible pathways for chromate conversion chemistry on zinc metal surfaces:<sup>2</sup>



Kulinich *et al.* reported that the thin film formed on the metal surface includes small amounts of hexavalent chromium species that could be  $\text{CrO}_4^{2-}$ ,  $\text{CrO}_3$  or  $\text{Cr}_2\text{O}_7^{2-}$ .<sup>3</sup> They also proposed that the hexavalent chromium trapped in the coating formed on the metal surface has a “self-healing” ability, so during corrosion it is able to recoat affected sites by producing additional  $\text{Cr}(\text{OH})_3(\text{s})$  and  $\text{Cr}_2\text{O}_3(\text{s})$ .<sup>3</sup>

### 1.1 Disadvantages of hexavalent CCCs

Despite the fact that hexavalent CCC is a good corrosion inhibitor, there are some disadvantages of its use because it is carcinogenic.<sup>4</sup> These disadvantages are based on environmental, health and safety concerns as well as the legislation governing its usage.

### 1.1.1 Legislation governing use of carcinogens in British Columbia

WorkSafeBC regulations for using designated substances (carcinogens, sensitizers, etc.) state that<sup>3</sup>:

1. *If a substance is identified as a designated substance, the employer must replace it, if practicable, with a material which reduces the risk to workers.*
2. *If it is not practicable to substitute a material which reduces the risk to workers, the employer must implement an exposure control plan to maintain workers' exposure as low as reasonably achievable below the exposure limit.*
3. *The plan must be reviewed at least annually and updated as necessary by the employer, in consultation with a health and safety representative, as applicable. The exposure control plan must incorporate the following elements:*
  - (a) a statement of purpose and responsibilities;*
  - (b) risk identification, assessment and control;*
  - (c) education and training;*
  - (d) written work procedures, when required;*
  - (e) hygiene facilities and decontamination procedures, when required;*
  - (f) health monitoring, when required;*
  - (g) documentation, when required.*

### 1.1.2 Health effects of hexavalent chromium

As per the WorkSafeBC regulations, the exposure limits in air for water soluble and insoluble hexavalent chromium are 0.025 mg/m<sup>3</sup> and 0.01 mg/m<sup>3</sup> respectively for a normal 8 hour work period.<sup>4</sup> Exposure to hexavalent chromium may result in the following health problems<sup>4</sup>:

- Lung cancer;
- Lung, nose and throat irritation if hexavalent chromium is breathed at high levels;
- Skin or eye irritation at high concentrations, such as 20 to 25 ppm of hexavalent chromium.

## 1.2 Hexavalent CCC alternatives

Some alternatives in existence include cerium oxide, phosphate, tungstate, zirconate, titanate, molybdate and vanadate coatings as well as trivalent chromium compounds.<sup>5</sup> Aramaki *et al.* reported that cerium chloride and cerium nitrate solutions were effective corrosion inhibitors when used on a zinc metal surface.<sup>6</sup> Shashikala *et al.* conducted a salt spray test as per the American Society for Testing and Materials (ASTM) B117 standard, to evaluate the corrosion performance of cerium oxide and chromate conversion coating using magnesium alloy as a substrate.<sup>7,9</sup> They reported that after 70 hours, white patches were formed on the substrate coated with chromate whereas for the substrate coated with cerium oxide, white patches were apparent after 28 hours.<sup>8</sup> This result implies that hexavalent chromium coatings have better corrosion resistance than cerium oxide coatings.

Phosphate conversion coatings are composed of crystalline salts of the substrate undergoing treatment, for example the formation of a zinc phosphate coating when zinc metal is used as a substrate.<sup>9</sup> Phosphates are widely used to improve the corrosion resistance of a metal when employed as a base for organic coatings; but when used without organic coatings, hexavalent chromium coating is applied over phosphate coating for better corrosion resistance.<sup>10</sup>

Zirconate and titanate based coatings are used as adhesives and corrosion inhibitors on aluminium metal surfaces; but without the use of a paint finish their corrosion resistance is poor when compared with hexavalent chromium coating.<sup>11</sup> Vanadate coating also provides moderate corrosion protection to metals, such as zinc and is relatively toxic but not as much as hexavalent chromium.<sup>10,11</sup>

In 1944, a US patent described the use of molybdenum based systems in the hexavalent state as a conversion coating material capable of replacing hexavalent CCC, but Bresline *et al.* compared the coating efficiency of sodium molybdate and sodium dichromate on aluminium alloys and reported that dichromate coatings were better than the molybdate coatings due to the strong oxidizing power of dichromate.<sup>12,13</sup>

Cowieson *et al.* reported a conversion coating treatment for tin-zinc alloy using tungstate systems.<sup>14</sup> As per their report, the corrosion resistance of tungstate coatings is analogous to molybdate coatings. However, when compared with hexavalent coatings in a corrosion test using salt spray, tungstate coatings provided a lesser degree of protection.<sup>15</sup>

In addition, Almeida *et al.* conducted a salt spray test to evaluate the corrosion performance of molybdate, tungstate, vanadate and hexavalent chromium coating on a zinc substrate.<sup>15</sup> They reported that it took 350 hours for 10% red rust to occur on the zinc substrate coated with hexavalent chromium coating but for molybdate, tungstate and vanadate coating it took only 85 hrs, 26 hrs and 30 hrs respectively for the same level of rusting.<sup>16</sup> This proved that hexavalent chromium coating has a better corrosion resistance than molybdate, tungstate and vanadate coating.

Trivalent chromium conversion coating has been used most prevalently as a replacement for hexavalent chromium systems, since Barnes *et al.* developed a trivalent chromium conversion coating system for zinc metal surfaces.<sup>16</sup> Trivalent chromium based conversion treatments are preferred over hexavalent chromium based systems in that they are not carcinogenic.<sup>5</sup> The trivalent chromium conversion coating solutions are primarily employed in the form of chromium nitrate.<sup>17</sup> Gardner *et al.* compared trivalent coatings with hexavalent coatings in relation to their corrosion resistance. They reported that after a thermal shock, the hexavalent coatings diminish more significantly than the trivalent coatings; but in a salt spray test, the corrosion resistance of hexavalent coatings is better than that of trivalent coatings.<sup>17</sup>

Given that hexavalent chromium coating has better corrosion resistance when compared with the alternatives mentioned, we opted to use hexavalent chromium in this study. Furthermore, in this study, we demonstrate a safe protocol for the use of hexavalent chromium in conversion coating using zinc plated metals and as well, a simple zinc plating procedure.

## 2.0 Experimental design

All reagents were obtained from Sigma-Aldrich or Alfa Aesar; zinc plated washers and fasteners were supplied by Rainhouse Ltd, Canada. A commercial hexavalent chromium test kit (HI 3846 chromium test kit) was purchased from Hanna Instruments, Inc., Canada.

### 2.1 Chromate conversion process

#### 2.1.1 Chromic acid bath preparation

An orange aqueous solution of  $K_2Cr_2O_7$  (200 g/l) was prepared by dissolving 20 g of potassium dichromate in a 500 ml beaker using 100 ml distilled water and stirred with a glass rod (does not dissolve completely until addition of the aqueous sulphuric acid). A colourless 0.6% v/v sulphuric acid solution was prepared by adding 0.6 ml of sulphuric acid (18.4 M, 98%) to approximately 100 ml distilled water in a volumetric flask (acid to water not water to the acid).<sup>18</sup> Both solutions were mixed at room temperature using a glass rod to make a chromic acid bath (orange in colour) in a one litre high density polyethylene (HDPE) container. Throughout the process, safety glasses, dust mask and nitrile/butyl rubber gloves should be used in a fume hood considering the powdery nature of the potassium dichromate.

#### 2.1.2 Coating process

Zinc plated washers were cleaned in a 500 ml beaker with soapy water (5 g of Sparkleen™ in 200 ml distilled water) and thoroughly rinsed with distilled water. A 22 American Wire Gauge (AWG) copper wire was used to hang the zinc plated washers to enable immersion in the chromic acid bath. The zinc plated washers were submerged in the chromic acid bath and swirled for 1 to 50 seconds at room temperature. This procedure was done with two washers for reproducibility.

The zinc plated washers were removed from the chromic acid bath and rinsed by immersion and agitation (swirling) in two separate distilled water baths (1 minute rinse per bath). After rinsing, the zinc plated washers were air dried for 24 hrs to allow hardening of the coating. In addition, the coating process was applied to zinc plated fasteners. A yellow iridescence emerged as the metal part slowly dried.

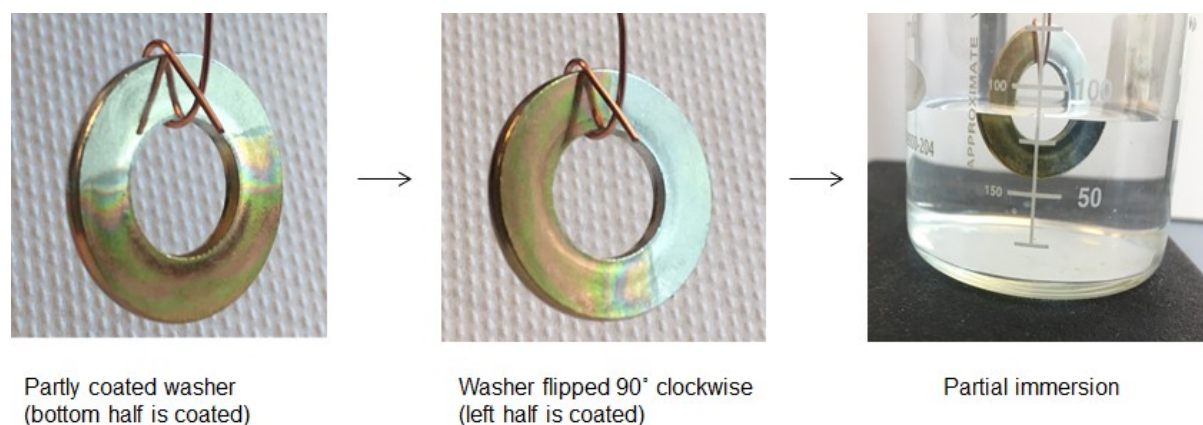
### 2.2 Chromic acid bath evaluation

The coating efficiency of chromium baths were evaluated by 5 seconds of immersion of the washers into variably reduced hexavalent chromium solutions. Eight solutions were prepared ranging from 0% to 100% reduced hexavalent chromium with 0.5 M sodium bisulphite (see 2.4 for full description).

## 2.3 Corrosion test

As per the ASTM B117, a salt spray test is used to simulate corrosion performance of metals. In this process, 5% NaCl aqueous solution is sprayed in a closed chamber to provide a corrosive setting for the metals to be evaluated.<sup>8</sup> In this study, seawater was used to replace the salt spray test because the metal pieces are designed for submarines; and also, to determine any correlation with the ASTM B117 standard.

The corrosion performance of hexavalent chromium coating was evaluated by immersing two partly coated washers in seawater. The first and second washer was partly coated by 5 seconds and 50 seconds immersion respectively in the chromic acid bath. Both washers were rotated 90° and immersed in seawater; so that an uncoated and a coated part are exposed to air and the other fraction is exposed to the seawater (see Figure 2). This was done to assess corrosion of the fraction in seawater as well as comparing with the parts exposed to air. The experiment lasted for 300 hours.



**Figure 2.** Representation of corrosion test.

## 2.4 Reduction of hexavalent chromium to trivalent chromium prior to disposal

A colourless 1 M sodium bisulphite solution was prepared by dissolving 5 g of sodium bisulphite in a 50 ml volumetric flask and filling with distilled water. The orange hexavalent chromium bath was reduced to a green trivalent chromium bath by adding 20 ml of 1 M sodium bisulphite to 10 ml of 0.5 M chromic acid (chromic acid used for coating) in a 100 ml beaker. It should be noted that at this stage, the sludge produced contains trivalent chromium, which is relatively non-toxic but a heavy metal. Heavy metals have to be controlled in order to avoid any form of environmental pollution as per Environment and Climate Change regulations in Canada.<sup>19</sup> Thus, Troy Hasanen (Occupational Health, Safety and Environment consultant for University of Victoria) recommended that the sludge should be properly disposed through a hazardous waste management facility, such as Aevitas which is located in Maple Ridge, British Columbia.<sup>20</sup>

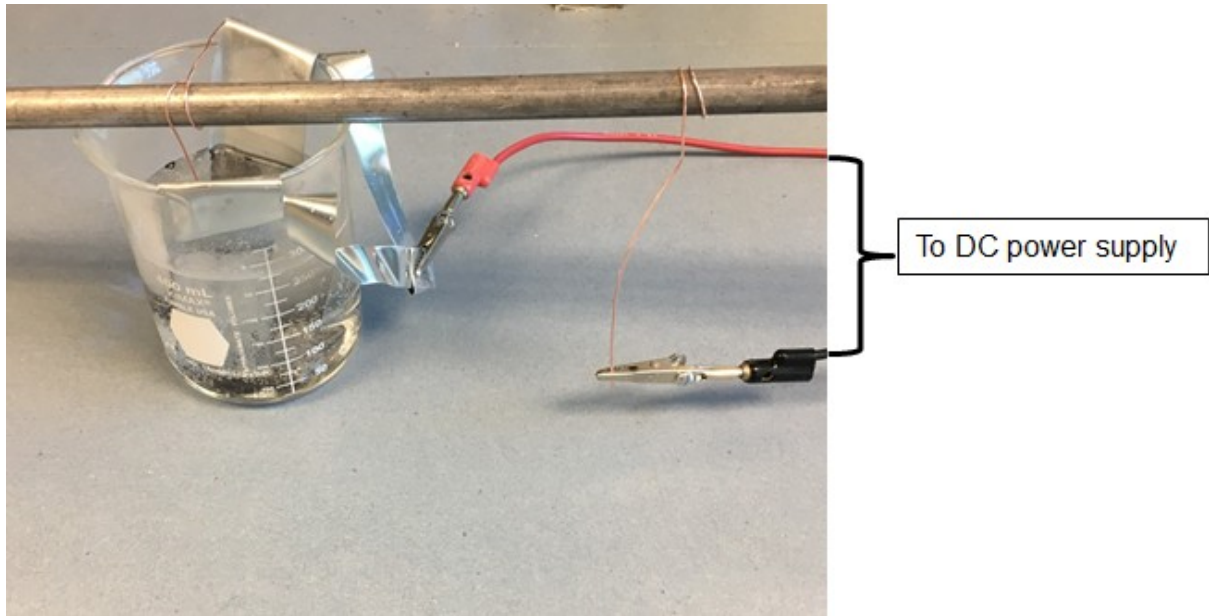
After the reduction process, it was necessary to verify the absence of hexavalent chromium by conducting a qualitative test using 1,5-diphenylcarbazide as the test reagent, which is

widely used for hexavalent chromium test due to its ability to detect hexavalent chromium at 10 ppb.<sup>21,22</sup> The qualitative test was carried out by adding 1 ml of 20 mM test reagent (0.4 g of 1,5 diphenylcarbazide in 80 ml acetone) to 100  $\mu$ l of the 90% and 100% reduced hexavalent chromium bath(see section 3.4 for colour description). A commercial hexavalent chromium test kit was also used for the qualitative test for hexavalent chromium. According to the procedure, concentrations of hexavalent chromium within the range of 0 to 1 ppm can be observed as purple coloured solutions of different intensity; in relation to this, reduced hexavalent chromium baths (70%, 80%, 90% and 100%) were examined per the procedure in the instruction manual of the test kit.

## 2.5 Zinc plating procedure

A colourless 5% v/v of acetic acid was prepared by adding 15 ml of acetic acid to approximately 300 ml of distilled water in a beaker; 30 g of magnesium sulphate (white powder) was dissolved in the 300 ml acetic acid to complement the electrolyte.<sup>23</sup>

A steel washer was degreased with soapy water (5 g of Sparkleen™ in 200 ml distilled water) and rinsed thoroughly with distilled water. The zinc foil (anode) was cut into two parts and placed into the electrolyte on opposite sides of the beaker (see Figure 3). This was done to allow a uniform electrodeposition of the zinc ions on the both sides of the steel washer. The zinc anodes were connected to each other and a 22 AWG copper wire was used to connect the anode to the positive side of the power supply. Aluminium tubing was installed on the top of the beaker; the steel washer was hung on a copper wire and attached to the aluminium tubing (this forms the cathode). The next step involved a complete submersion of the steel washer in the electrolyte. Another wire was connected from the cathode to the negative side of the DC power supply. The DC power supply was turned on and a voltage and current of 3 V and 0.3 A respectively were employed for the plating. In order to test the effectiveness of the process, the plating was stopped after 10 minutes for a brief inspection of the steel washer; a grey colour was observed on the surface of the washer on both sides. Plating was complete within 30 minutes.<sup>23</sup>



**Figure 3.** Zinc plating set-up.

After plating, the DC power supply was unplugged and the washer was removed from the electrolyte; rinsed with distilled water, dried with a blow dryer and polished using a steel wool.<sup>23</sup> After polishing, a bright silver coloured surface was observed and the zinc plated washer was washed in soapy water and rinsed with distilled water (see Figure 4).



Before plating



After plating



Zinc plated washer (after polishing)

**Figure 4.** Zinc plating from uncoated steel to polished zinc plated washer.



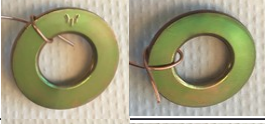
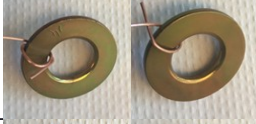
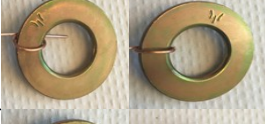
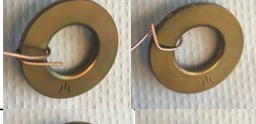
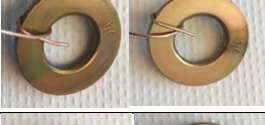
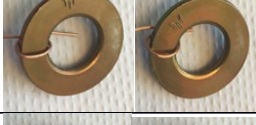
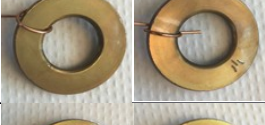




### 3.0 Results and Discussion

#### 3.1 Chromate conversion coating

As shown in Table 1, short immersion times (1-15 seconds) produced a light yellow iridescent colour whereas long immersion times produced a dark yellow iridescent colour. Also, poor coating can be observed for samples with immersion time from 35 to 50 seconds. This could be explained by poor adhesion of the outer layers as a result of the thickness of the coating.<sup>1</sup>

**Table 1.** Representation of coated samples in relation to their immersion time.

Immersion time (seconds)	Sample	Immersion time (seconds)	Sample
1		5	
10		15	
20		25	
30		35	
40		45	
50			

#### 3.2 Coating Evaluation

According to the ASTM B201-80 standard, the simplest way to evaluate the coating is through visual inspection, where the smoothness and adhesion of the coating can be observed.<sup>24</sup> In this study, the washers immersed from 5 to 15 seconds in the chromic acid passed the visual inspection. The washers immersed from 20 to 50 seconds exhibited poor

adhesion; hence, failed the visual inspection. In addition, two coated fasteners (control) from Rainhouse, Ltd were compared with coated washers (5 to 15 seconds immersion) and coated fasteners (5 seconds immersion). It was observed that the washer and fastener coated for 5 seconds have similar coating appearance as the control (see Figure 5). This implies that 5 seconds immersion time would suffice for coating.



A



B



C

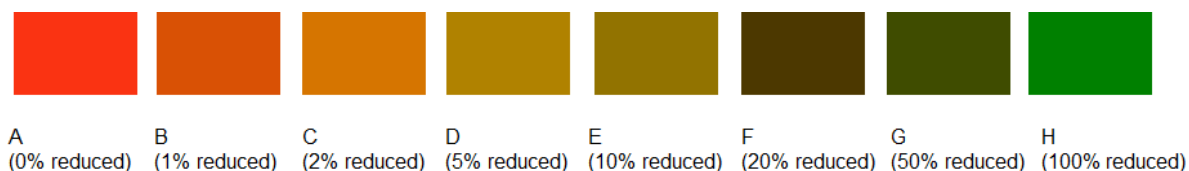


D

**Figure 5.** A and C are a description of coated fasteners from Rainhouse (control). B and D are a description of coated washer and fastener after 5 seconds immersion.

### 3.3 Chromic acid bath assessment

In order to determine when to change the chromic acid bath after several use, the coating efficiency of various baths containing different concentrations of hexavalent chromium were assessed. Figure 6 and Table 2 show a description of the assessment.



**Figure 6.** Representation of various chrome baths with decreasing hexavalent chromium content from A to H.

**Table 2.** Representation of samples after 5 seconds of immersion in the chrome bath.

Chrome bath used	A	B	C	D	E	F	G	H
Samples								

After coating the metal parts using A to D (0% to 5% reduced hexavalent chromium baths respectively), the coated samples appeared well-coated with a shiny iridescent colour and good adhesion; hence, passed the coating evaluation. However, as the hexavalent chromium is further reduced to trivalent chromium, that is, from E through H, the iridescent look disappears. This implies that, when a chromic acid bath resembles E to H, it should be replaced with a new bath for good results.

### 3.4 Qualitative test for hexavalent chromium

In the presence of hexavalent chromium, a purple colouration is observed after a reaction with 1, 5 diphenylcarbazide.<sup>25</sup> This can be attributed to the oxidation of the test reagent to diphenylcarbazone and the reduction of hexavalent chromium to trivalent chromium in the process. The complexation between trivalent chromium and diphenylcarbazone results in the purple colouration.<sup>25</sup>

Upon addition of the test reagent to a 90% and 100% reduced hexavalent chromium bath samples (both had green colouration confirming presence of trivalent chromium), the former

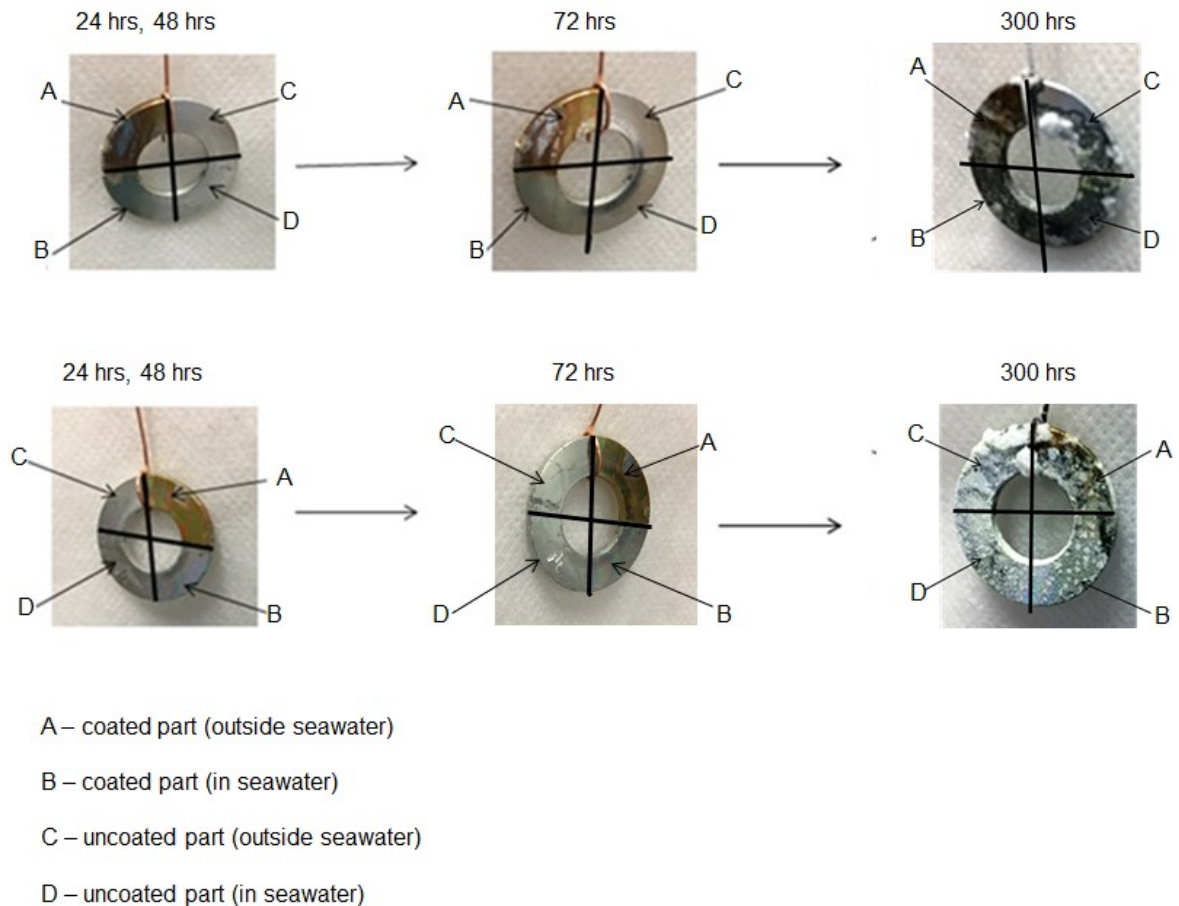
turned purple whereas in the latter, a white precipitate (chromium diphenylcarbazide complex) was formed.<sup>25</sup> This observation proved the absence of hexavalent chromium in the 100% reduced hexavalent chromium bath after the reduction process.

In the test using the chromium test kit, there was no detection of hexavalent chromium in the 80% and 90% reduced bath; but a purple colouration was observed in the 70% reduced hexavalent chromium bath which indicated the presence of hexavalent chromium. Thus, the qualitative test using 1,5-diphenylcarbazide test reagent is more sensitive than using the chromium test kit in that it is able to detect hexavalent chromium in a 90% reduced bath.

### 3.5 Corrosion test

According to the ASTM B117 standard, in a typical salt spray test, a white corrosion will appear approximately 8 hours for uncoated zinc plated metal and 200 hours for an iridescent yellow coated metal; but in seawater it appears there is poor correlation.<sup>1</sup> This is evident in Figure 7, which shows no corrosion at 72 hours for the uncoated part but the occurrence of white corrosion is observed at 300 hours. Although the salt spray test shows poor correlation when compared with corrosion test in seawater, it is useful in assessing coating processes, such as electroplating, galvanizing and painting in that it produces rapid results.<sup>1</sup>

In addition, as indicated in Figure 7, the washer at the top right corner is partly covered with white corrosion whereas the washer below it is all covered with white corrosion at 300 hours. This can be attributed to longer immersion time (50 seconds) for the partial white corrosion, and as such has a thicker coating, which delays white corrosion. This does not imply that thicker coatings are superior in quality because they easily turn powdery when stress is applied. However, hexavalent chromium coated metal parts in application are secured in place and reinforced with paint coatings, such as epoxy and polyurethane coatings, in order to further delay corrosion.<sup>26</sup>



**Figure 7.** Description of corrosion process at 24 hrs, 48 hrs, 72 hrs and 300 hrs.

## 4.0 Conclusions

CCC is an efficacious and fast means of protecting metal parts from corrosion, but problematic in that it uses the toxic and carcinogenic chromic acid as the reagent. If CCC is the only option, some key considerations:

1. The coating efficiency of the bath is dependent on the extent of reduction of hexavalent chromium, and more than 10% reduced solutions no longer provide good results. The degree of reduction is visually indicated by a colour change from red to brown (and eventually to green).
2. Five seconds immersion time is sufficient for good adhesion and excellent quality coating.
3. Coatings produced from long immersion time have a better corrosion resistance than coatings produced from short immersion time.
4. There is no significant difference between chromate conversion coating done immediately and later after zinc plating; but ensuring that a clean surface of the substrate is used for coating leads to the production of good coatings.

5. Hexavalent chromium bath is safe for disposal after the reduction of hexavalent chromium (6+) to trivalent chromium (3+) using an excess of sodium bisulphite reducing agent.

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