



## Effects of Trivalent Chromium Thiocyanate and Operating Parameters on the Throwing Power and Corrosion Resistance for Trivalent Chromium Electrodeposition

Nurul Aidilla Nahrawi<sup>a</sup>, Che Rozid Mamat<sup>b</sup>, Aishah Abdul Jalil<sup>c</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia 81310 Johor Bahru, Malaysia

<sup>b</sup>Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia 81310 Johor Bahru, Malaysia

<sup>c</sup>Centre for Hydrogen Energy, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia

Corresponding author: aidilla@uyemura.co.jp, che@kimia.fs.utm.my, aishahaj@utm.my

### Abstract

Chromium plating is used in various applications due to excellent corrosion performance and wear resistance. Conventional chromium plating containing toxic hexavalent chromium was restricted to use and led to trivalent chromium plating system as an alternative. A chromium-based electrolyte containing predominantly trivalent chromium as chromium source was discovered showing a bright chromium appearance with high corrosion resistance. However, low throwing power makes it impossible to generate a uniform distribution of chromium deposits over substrate. The present work aims at throwing power improvement of trivalent chromium electrolyte by use of additive, trivalent chromium thiocyanate using Hull cell method. The effect of different factors such as pH, temperature and current density was investigated at optimum concentration of additive. The corrosion resistance was tested using Accelerated Salt Spray. The chromium deposit exhibits a bright appearance with higher deposit thickness. The throwing power of trivalent chromium electrolyte was found to improve with the increase of additive concentration. At optimum additive concentration, 6% v/v the throwing power was shown to improve at pH 2.20, temperature 40 °C and current density 0.10 Am<sup>-2</sup>. Accelerated corrosion tests proved that the trivalent chromium electrolyte with additive had high corrosion protection and was comparable to the electrolyte with free additive.

**Keywords:** Decorative trivalent chromium; trivalent chromium thiocyanate; throwing power; corrosion resistance

### Introduction

Decorative trivalent chromium electrodeposition is among the most common plating processes used as a metal finishing, particularly in automotive and appliances [1]. The chromium deposit has a shiny appearance when coated on the metal and is used as a protective layer due to its high hardness and corrosion resistance. Traditional chromium plating is produced from hexavalent chromium electrolyte which is known as a highly toxic and carcinogenic chemical that is extremely hazardous to both humans and the environment [2]. Because of this, trivalent chromium coating has been introduced as an alternative thus a new direction in decorative plating has been established.

A chromium-based electrolyte containing predominantly trivalent chromium as chromium source, organic carboxylate ions as a complexing agent, and sulphate ions as a conductivity salt were used in this study. It was discovered that has a shiny bright chromium appearance as well as high corrosion resistance and hardness deposit qualities [3]. However, there is a performance constraint due to the disadvantage of inadequate throwing power in the recess region of the article, which makes it impossible to generate uniform chromium thickness for equal protection. Good throwing power, giving increased thickness at regions of low current density, is particularly important when the article is applied mainly to protect against corrosion since corrosion usually occurs in the thinnest area [4]. To improve the throwing power of decorative trivalent chromium plating, the trivalent chromium thiocyanate based was employed in the electroplating solution as an additive. It was reported may enhance the chromium reduction at the cathode surface, resulting in a bright color deposit, improve plating efficiency and plating range [5].

In brief, the present work aims at investigating the influence of trivalent chromium thiocyanate additive on the throwing power of a trivalent chromium-based electrolyte, using the Hull cell test. The effects of operational conditions such as pH, temperature, and current density were examined to determine the optimum deposit plating range. Finally, the corrosion resistance of this developed trivalent chromium solution with additive was tested using the Accelerated Salt Spray test.

**Materials and methods**

The experiment was divided into two (2) sections which are throwing power measurement and corrosion test. For throwing power, a 0.0130 m<sup>2</sup> brass substrate was cleaned using C-4000T, activated using hydrochloric acid 30 % v/v, plated with nickel before chromium plating using Hull Cell. The nickel solution consists of 150 – 300 gL<sup>-1</sup> NiSO<sub>4</sub>.6H<sub>2</sub>O, 60 – 150 gL<sup>-1</sup> NiCl<sub>2</sub>.6H<sub>2</sub>O, 37 – 52 gL<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>, 14 mL<sup>-1</sup> HEBAT NICKEL AB-30, 0.8 mL<sup>-1</sup> HEBAT NICKEL AB-40 and 1 mL<sup>-1</sup> HEBAT NICKEL AW-2R. The nickel plating was operated at temperature 50.0 °C, pH 4.20 – 4.60 and current density 0.04 Am<sup>-2</sup> for 5 min with nickel anode.

For chromium plating, various concentration of additive (0, 2, 4, 6 and 8 %v/v) was added into the basic trivalent chromium solution, HEBAT CHROME CLH-1. The Hull cell tests were conducted using a standard 1000 mL Hull cell and the chromium plating solutions were tested at temperature 40.0 °C, current density 0.10 Am<sup>-2</sup>, pH 2.20 for 3 min using iridium oxide anode. The optimum concentration of additive was further tested at variable operating parameters such as pH, temperature and current density. From the Hull cell substrate, the chromium deposit appearance across current densities was interpreted by visual observation and classified as burnt, bright, black streak, and uncoated. The length of brightness was measured by a ruler.

The chromium deposit thickness on Hull cell substrate was measured using X-ray fluorescence (XRF) at the middle area of the chromium plated substrate at various horizontal distances. The throwing power was determined by measuring and compared the ratio of deposit thickness between high current density area (HCD) and low current density area (LCD). The HCD area was specified as an area 0.0170 m from the left border of the Hull cell panels and the LCD as an area 0.0230 m from the right border of the Hull cell panels. The LCD and HCD regions of 10 A panel corresponds to a local current density of 0.05 Am<sup>-2</sup> and 0.40 Am<sup>-2</sup>, respectively. The low HCD/LCD ratio refers to low thickness differences between high and low current density regions, indicating good throwing power.

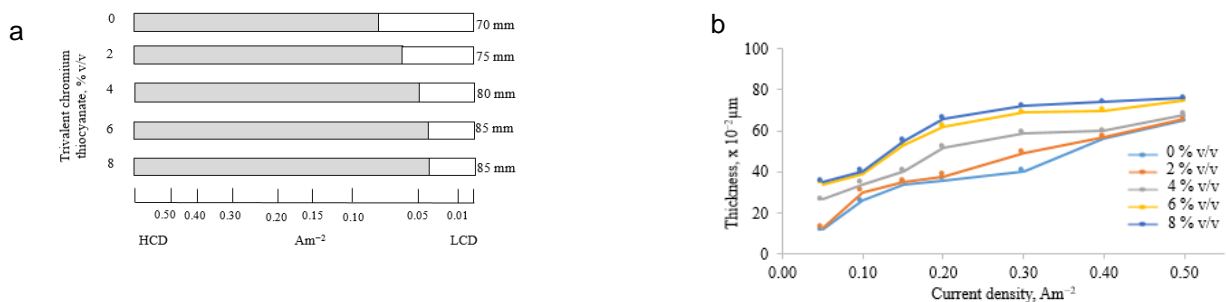
For corrosion test, a 0.0040 m<sup>2</sup> acrylonitrile butadiene styrene (ABS) sample with hexavalent chromium finishing was stripped using a mixture of 50 gL<sup>-1</sup> sodium hydroxide and 5 gL<sup>-1</sup> C-4000T for 5 min at room temperature with voltage of 5V. The chromium plating was plated onto the ABS sample using basic trivalent chromium electrolyte with variable concentration of additive (0, 2, 4, 6 and 8 %v/v) and corrosion test was carried out in accordance with the methods outlined in the Japan Industrial Standard for corrosion testing of metallic coatings, JIS H 8502.

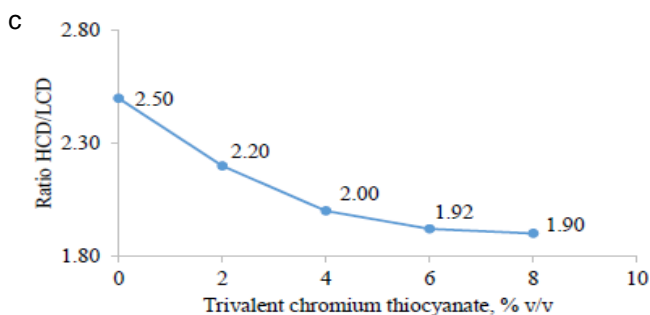
**Results and discussion**

Throwing power measurement

a) Effect of variable concentration additive

The chromium deposit obtained from the basic trivalent electrolyte was bright, with plating lengths of 70 mm across current densities. The trivalent chromium thiocyanate concentration was varied from 0 to 8 % v/v. The presence of trivalent chromium thiocyanate concentrations ranging from 2 % v/v to 6 % v/v resulted in a significant improvement in chromium bright plating length, increasing from 70 to 85 mm. Further increase in trivalent chromium thiocyanate up to 8 % v/v does not affect the chromium plating length. The thickness of the chromium deposit was measured using XRF and the result shows an increase of trivalent chromium thiocyanate additive in the basic trivalent chromium solution, from 2 % v/v to 8 % v/v improved the deposit thickness across various current densities. It was found a decreasing trend of HCD/LCD ratio, from 2.50 to 1.90 was observed for 0 % v/v to 8 % v/v which is referred to improved throwing power when compared to the basic trivalent chromium. The significant improvement in the brightness range, deposit thickness, and increase in the throwing power in low current density areas with bright colour deposits proved that the trivalent chromium thiocyanate affected trivalent chromium reduction at the cathode surface [6]. However, when the additive concentration was increased from 6 to 8% v/v, there was no improvement in brightness coverage, deposit thickness, or throwing power [7]. As a result, the additive concentration of 6% v/v was determined to be optimal. The brightness coverage, deposit thickness and HCD/LCD ratio at various concentrations of additive are depicted in Figure 1.

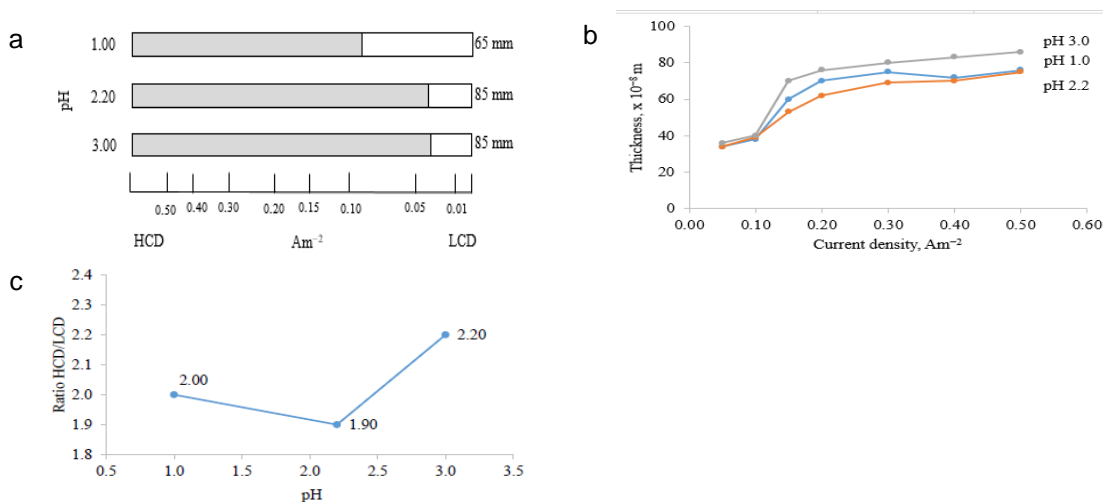




**Figure 1** Effect of various concentration of additive on brightness coverage (a); thickness (b); and HCD/LCD ratio (c).

b) Effect of variable pH

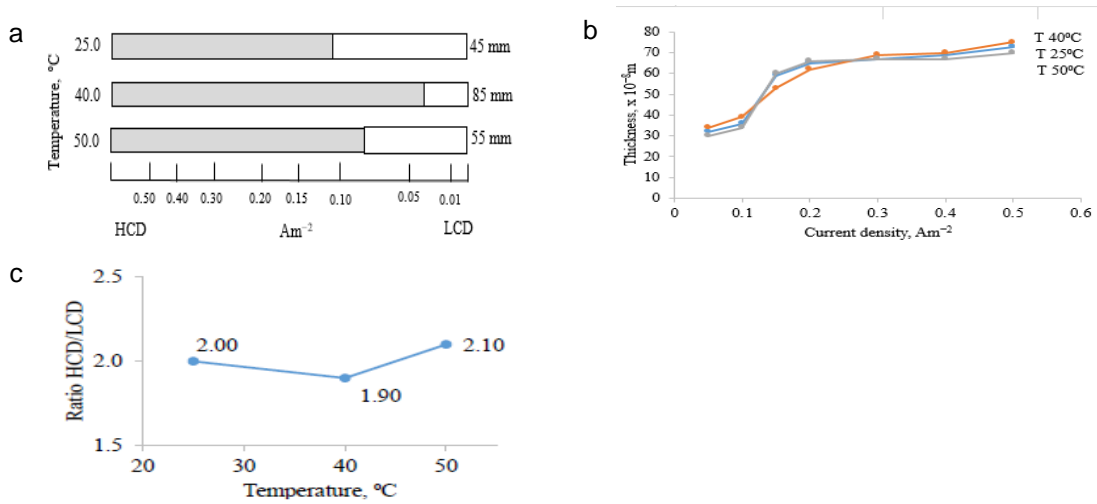
At the optimum additive concentration of 6% v/v, the smooth and adhere chromium deposit was plated over the substrate at pH 1.00, pH 2.20 and pH 3.00. The brightness range was found to be comparable at pH 2.20 and pH 3.00. At pH 1.00, the brightness range was found lower. The chromium deposit thickness was found higher at pH 1.00 and pH 3.00, compared to pH 2.20. For throwing power, a higher ratio of HCD/LCD was observed at pH 1.00 and pH 3.00, compared to pH 2.20. Based on the findings, pH 2.20 was determined to be optimal. Figure 2 shows brightness coverage, deposit thickness and HCD/LCD ratio at variable pH of trivalent chromium plating solution with an optimal concentration of additive.



**Figure 2** Effect of various pH additive on brightness coverage (a); thickness (b); and HCD/LCD ratio (c)

c) Effect of variable temperature

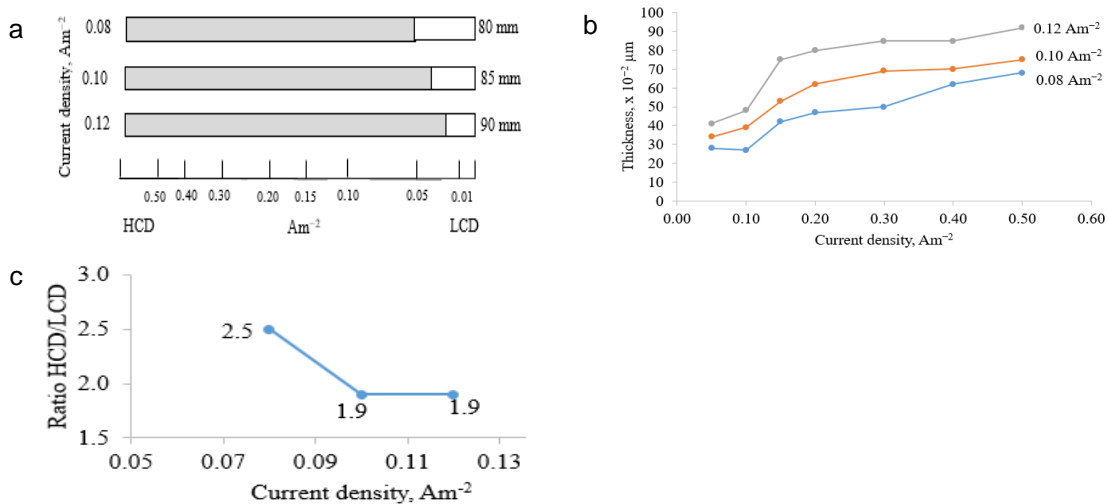
The chromium deposit produced at 40.0 °C had a brightness range of 85 mm. The brightness range of the chromium plating was reduced from 85 mm to 45 mm and 55 mm, respectively, when the temperature was dropped to room temperature or elevated to 50.0 °C. Temperature 40.0 °C produced a thicker chromium deposit than temperature 25.0 °C. While temperature 50.0 °C has the lowest thickness trend. The HCD/LCD ratio was determined using the distribution thickness data and it was discovered that temperatures 25.0 °C had a greater HCD/LCD ratio than temperatures 40.0 °C and 50.0 °C. The HCD/LCD ratio was found to be equal at temperatures 40.0°C and 50.0°C. Temperature 40.0°C provides a higher deposit thickness and brightness coverage with a lower HCD/LCD ratio when taking into account brightness range, deposit thickness, and throwing power. According to our observations, the ideal temperature is 40.0 °C. The brightness coverage, deposit thickness and HCD/LCD ratio at various concentrations of additive are depicted in Figure 3.



**Figure 3** Effect of various temperature on brightness coverage (a); thickness (b); and HCD/LCD ratio (c)

d) Effect of variable current density

The effect of current density on the trivalent chromium plating was evaluated at an optimum trivalent chromium thiocyanate concentration. It was found that the bright chromium deposit improved from 80 mm to 90 mm at current densities ranging from 0.08 to 0.12  $\text{Am}^{-2}$ . The thickness of the chromium deposit was observed to increase as the current density increased. The HCD/LCD ratio of 0.08  $\text{Am}^{-2}$  current density was higher than 0.10  $\text{Am}^{-2}$  and 0.12  $\text{Am}^{-2}$  current density. The HCD/LCD ratio was found to be equal at the current density 0.10  $\text{Am}^{-2}$  and 0.12  $\text{Am}^{-2}$ . The cathode current density should be as low as possible, hence, the best current density is 0.10  $\text{Am}^{-2}$ . Figure 4 shows brightness coverage, deposit thickness and HCD/LCD ratio at variable pH of trivalent chromium plating solution with an optimal concentration of additive.



**Figure 4** Effect of various current density on brightness coverage (a); thickness (b); and HCD/LCD ratio (c)

Corrosion test

The accelerated salt spray testing was performed to demonstrate the compatibility of chromium metal as a protective layer in accelerated atmospheric corrosion. The ABS sample has a multi-layered metal plating, such as microporous nickel to provide corrosion protection [8]. The 0.4  $\mu\text{m}$  chromium deposit from the trivalent chromium plating solution at a variable concentration of additive, ranging from 0% v/v to 8% v/v, was plated over the nickel layer on the ABS sample. The salt spray test was carried out continuously over a period of 80 h with assessing the rating number every 16 hours.

The hexavalent chromium sample and trivalent chromium sample with and without additive have no corrosion marks or discolouration from 16 h to 64 h of exposure to the salt spray solution. As a result, it was graded with a rating number 10. After 80 h of salt spray test, the corrosion pit marks were identified for the hexavalent chromium sample and the corrosion rating number was 9 since the substrate was still coated. For trivalent chromium plating solution with free additive, the corrosion rating number was maintained at 10 due to no discolouration or corrosion marks observed. The presence of an additive, ranging from 2% v/v to 8% v/v results in a similar appearance and rating number to the trivalent chromium plating solution-free additive. The hexavalent chromium plating consists of chromium deposits with a low concentration of hydrogen, has a crack surface type due to releasing of hydrogen from chromium deposit during the electroplating process. The trivalent chromium plating solution contains organic carboxylate as a complexing agent, containing chromium deposits with carbon carbides [9]. It produces a surface crack-free type, resulting in higher corrosion resistance than hexavalent chromium plating solution [10].

**Table 1:** The salt spray rating number for hexavalent chromium and trivalent chromium with or without additive

No.	Sample	Rating number (h)					
		0	16	32	48	64	80
1	Hexavalent chromium (0.4 µm)	10	10	10	10	10	9
2	Trivalent chromium (0.4 µm)	10	10	10	10	10	10
3	Trivalent chromium with 2 % v/v trivalent chromium thiocyanate (0.4 µm)	10	10	10	10	10	10
4	Trivalent chromium with 4 % v/v trivalent chromium thiocyanate (0.4 µm)	10	10	10	10	10	10
5	Trivalent chromium with 6 % v/v trivalent chromium thiocyanate (0.4 µm)	10	10	10	10	10	10
6	Trivalent chromium with 8 % v/v trivalent chromium thiocyanate (0.4 µm)	10	10	10	10	10	10

**Conclusion**

The inclusion of trivalent chromium thiocyanate additive improves the shiny bright throwing power over the sample substrate in the trivalent chromium electrolyte. The optimal concentration of trivalent chromium thiocyanate was 6 % v/v at pH 2.20, temperature 40°C, and a current density of 0.10 Am<sup>-2</sup>. There were no changes in the chromium deposit because of the excellent corrosion resistance, which was comparable to a trivalent chromium electrolyte with no additives.

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