



The hazardous hexavalent chromium formed on trivalent chromium conversion coating: The origin, influence factors and control measures

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ABSTRACT

In this paper, the effects of processing parameters and constituents of treating-agent on the presence of hazardous hexavalent chromium on trivalent chromium conversion coating were studied. Results showed that shorter immersion time, lower bath pH value as well as lower working and baking temperatures retarded the presence of hexavalent chromium. In addition, the concentration of hexavalent chromium on conversion coatings prepared by the oxalic acid treating-agent was far greater than those on conversion coatings prepared by formic acid and acetic acid treating-agents. Results also indicated that the concentration of hexavalent chromium on conversion coatings was enhanced due to the addition of bivalent cobalt and nitrate anion in treating-agent, especially for oxalic acid conversion coating. However, the addition of hydroxyl compound D-gluconic acid in treating-agent could reduce the concentration of hexavalent chromium effectively. Moreover, a possible formation mechanism of hexavalent chromium on trivalent conversion coating was proposed. Findings of this study provide a better understanding of the formation of hexavalent chromium on trivalent chromium conversion coating and can facilitate the management of trivalent chromium treating-agents and trivalent chromium fasteners.

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1. Introduction

Although the hexavalent chromium surface treatment technology is a very effective anti-corrosion method, according to the Directives of European Union (EU) such as REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) and RoHS (Restriction of Hazardous Substances) [1–6], it can no longer be used in the field of surface treatment [7–10]. Consequently, due to the environmental and legislative pressure, the trivalent chromium surface treatment technology has been used as the preferential and green alternative for the time being and has also proven its excellence in anti-corrosion and decoration effects [8–10].

However, trace hexavalent chromium can be easily detected in trivalent chromium conversion coating, especially for iridescent conversion coating [11–14]. This new environmental issue about the safe and friendly trivalent chromium conversion coating has been argued and caused extensive controversy. The earlier report on this issue can be found in Rochester and Kennedy [11]. They put trivalent chromate samples into a salt fog chamber, and looked at the samples after a period of exposure. They concluded that the trivalent chromium could be oxidized to hexavalent chromium under certain conditions even though there was no oxidation agent.

Kennedy et al. [12] tried a fairly large number of trivalent chromium samples and found the similar behavior. Among the samples, some generated more hexavalent chromium while some less. At present, once hexavalent chromium of the trivalent chromium samples is identified by the Societe Generale de Surveillance S.A (SGS) or other authoritative testing bureaus, a large-scale return of products will be demanded by end-users. In view of these hot issues, people began to suspect the safety of trivalent chromium treating-agent. Therefore, a scientifically view of the formation origin, influence factors for hexavalent chromium conversion, and management of trivalent chromium treating-agent is very necessary [4,5].

In response to these problems, the objectives of this work are: (1) to compare the presence of hexavalent chromium on trivalent chromium conversion coatings prepared by different trivalent chromium treating-agents available; (2) to discuss the possible formation mechanism of hexavalent chromium; (3) to discuss the effect of the influence factors such as the processing parameters and the constituents of treating-agent on the presence of hexavalent chromium.

2. Experimental procedures and analytical methods

2.1. Fastener samples preparation

All passivated samples used in the experiment were fasteners with zinc metallic coating. Firstly, the treating-agent was diluted

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with deionized (DI) water to the required concentration. Then the pH value of the diluted treating-agent was adjusted with sulfuric acid (H₂SO₄) or sodium hydroxide (NaOH) to a designed value and heated to the working temperature. Afterwards, the DI-water-rinsed fasteners were immersed into the diluted solution for a period of time for coating and then dried at a proper baking temperature.

The concentration of hexavalent chromium on conversion coating changes drastically with time and storage conditions. In accordance with the requirements of analytical methods, the samples tested in the experiment were all stored under a constant ambient conditions (humidity 45–75 RH (relative humidity), temperature 15 °C).

2.2. Experimental procedures

Three types of experiments were carried out during this study: (1) four currently available trivalent chromium treating-agents were used to compare the presence of hexavalent chromium; (2) a trivalent chromium treating-agent was used to evaluate the effect of processing parameters on the presence of hexavalent chromium; (3) a self-developed treating-agent was used to evaluate the effect of its constituents on the presence of hexavalent chromium.

2.2.1. The comparison of commercial iridescent treating-agents

Four commercial iridescent treating-agents (JASCO TR-173A, Nippon Hyomen Kagaku Kabushiki Kaisha, Japan; MacDermid Spectramate™ 25, MacDermid American Co., Ltd., American; ST-301, Shanghai Sustain Co., Ltd, China; Jisheng A01-234C, Greenkem Chemical Technology Co., Ltd., China) with good corrosion resistance and high decorative performance were used. These treating-agents were first diluted according to the manufacturer's recommendations. Then the fastener samples were passivated under the optimized processing parameters. The alkaline-boiling-water-extraction method (SJ/T 11365-2006)[15] was used to determine the amount of hexavalent chromium on trivalent chromium conversion coating, which is recommended by the Electronic Industry Standard of People's Republic of China and has been recognized as a variant of the International Electrotechnical Commission (IEC) 62321[16].

2.2.2. The effect of processing parameters

A commercial iridescent treating-agent (ST-301) was chosen to investigate the effect of processing parameters. A series of fastener samples were prepared by varying the working temperature, bath pH value, immersion time and baking temperature of treating-agent, respectively. The IEC recommended spot-testing method (IEC 62321) was used for qualitative analysis of hexavalent chromium [16].

2.2.3. The effect of treating-agent constituent

Firstly, three kinds of self-developed iridescent treating-agents were prepared by varying the concentration of chromium sulfate, cobalt sulfate, sodium nitrate and D-gluconic acid. Then the fastener samples were passivated under the optimized processing parameters. The corresponding optimized constituents and processing parameters are listed in Table 1. All the chemicals used in the treating-agents are analytical grade and obtained from Shanghai Chemical Reagent Co. in China.

2.2.4. Control test

Apart from the passivated samples, the unpassivated zinc samples were also tested using the same procedure as the control samples.

Table 1

The optimized constituents and processing parameters of three iridescent treating-agents.

Parameters	Concentration (g/L)	
Complexing agent	Formic acid	40–50
	Acetic acid	40–50
	Oxalic acid	45–60
Chromium sulfate	45–60	
Cobalt sulfate	9–12	
Sodium nitrate	175–185	
D-gluconic	45–55	
Processing parameters		
pH	2.0	
Immersion time	25s	
Working temperature	25 °C	
Baking temperature	80 °C	

2.3. Salt spray corrosion tests

Salt spray corrosion tests were carried out according to the standard practice of ASTM B117 [17]. The percentage of the fastener samples' surface covered with white rust was evaluated at intervals of 12 h.

2.4. Analytical method of hexavalent chromium

The detailed process of spot-testing analysis (IEC 62321) [16] and the alkaline-boiling-water extraction analysis (SJ/T 11365-2006) [15] for hexavalent chromium determination are shown as below.

2.4.1. The spot-test procedure

- 1) For preparation of the test solution, 0.4 g of 1,5-diphenylcarbazine was dissolved in a mixture of 20 mL of acetone and 20 mL of ethanol. After the dissolution, 20 mL of orthophosphoric acid and 20 mL of DI water were added to the above solution.
- 2) A fastener sample was placed into a small container and then 1–5 drops of the test solution prepared in step 1 were added.
- 3) The test solution's change of color from red to violet was observed after the removal of the fastener sample from the container.

2.4.2. The alkaline-boiling-water-extraction procedure

- 1) For preparation of the test solution, 0.5 g of diphenylcarbazine was dissolved in 50 mL of acetone and 50 mL of DI water. This test solution was stored under refrigeration in an amber glass bottle.
- 2) The fastener samples with a total surface area of (50 ± 5) cm² were placed into a suitable beaker containing 50 mL of DI water and 0.2 mL of sodium hydroxide (1%).
- 3) The above beaker was heated to boiling for 2 min and then the solution in the beaker was transferred to a 50 mL glass bottles. The pH value of the solution was adjusted to 1.0–2.0 by adding 2 mL of nitric acid solution (10%).
- 4) The above solution containing 2 mL of orthophosphoric acid and 2 mL of test solution was analyzed at the wavelength of 540 nm using a UV 2102-PC spectrophotometer (Shanghai Unico Co., China).

In order to improve the sensitivity, a 5 cm absorption cell was used to get the lower limit of detection (LOD) 0.008 mg/L. The variation of replicated measurements was within 10% in all cases. Samples were examined at the intervals of 1, 2, 4, 8, 16, 24, and 30 days.

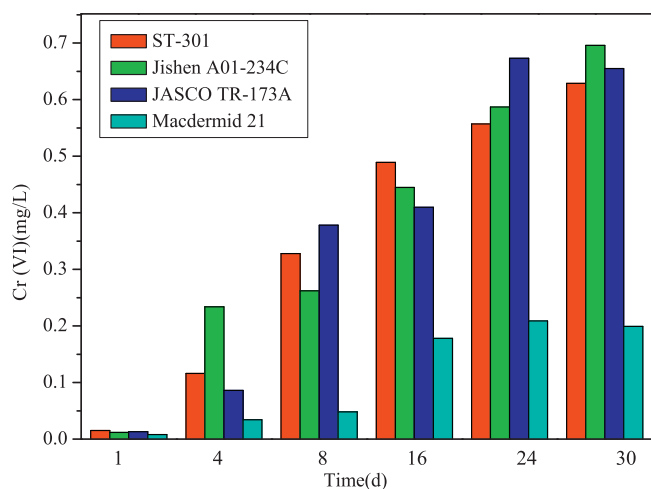


Fig. 1. The concentration of hexavalent chromium on conversion coatings prepared by different commercial iridescent treating-agents.

3. Results and discussion

3.1. The presence of hexavalent chromium on trivalent chromium conversion coating

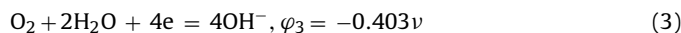
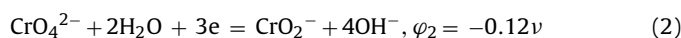
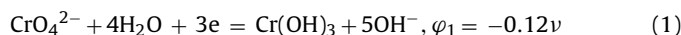
The relationship between the storage time of fastener samples and hexavalent chromium concentration on different conversion coatings is shown in Fig. 1. The hexavalent chromium could be easily detected on the four types of iridescent conversion coatings. Furthermore, the concentration of hexavalent chromium increased drastically with the increase of storage time. For example, the concentration of hexavalent chromium on ST-301 conversion coating was only 0.13 mg/L after 4 days and then increased rapidly to 0.63 mg/L after 30 days. Fig. 1 also presents that the Macdermid Spectramate™ 25 worked better than other treating-agents since the formation rate of hexavalent chromium was the lowest. After 30 days, the concentration of hexavalent chromium on Macdermid Spectramate™ 25 conversion coating was only 0.23 mg/L, while the concentrations of hexavalent chromium on other three types of conversion coatings (ST-301, Jisheng A01-234C, TR-173A) reached 0.63 mg/L, 0.70 mg/L, and 0.66 mg/L, respectively. The result indicates the presence of hexavalent chromium on different trivalent chromium conversion coatings and thus suggests that the processing parameters and constituents of treating-agent may be the important factors influencing the formation of hexavalent chromium.

3.2. The formation mechanism of hexavalent chromium on trivalent chromium conversion coating

The formation mechanism of hexavalent chromium is complicated and may be affected by many factors including the thermodynamics, dynamics properties of trivalent chromium ions as well as the microstructure of trivalent chromium conversion coating.

The trivalent chromium complexes, including the chrome hydroxide zinc cations and anions (as $\text{Cr}(\text{OH})_3$ or the hydrolysis of trivalent chromium form CrO_2^- present) are the major compounds of conversion coating. In the passivation process, the pH value obtained on the zinc layer increases due to the consumption of acid. The stable valence state of chromium ions is pH-dependent. In acidic conditions trivalent chromium is stabilized, while under alkaline conditions it is in the hexavalent state. The standard potentials of the probable half reaction occurring on trivalent chromium

conversion coating under alkaline conditions are described as in Eqs (1)–(3) [14].



As can be seen from above, the potential of (3) is much higher than those of (2) and (1), indicating that the trivalent chromium is probably oxidized to hexavalent chromium in the presence of oxygen and water. Therefore, the reduction of oxygen may be the main reason for the presence of hexavalent chromium on trivalent chromium conversion coating. Previous reported works have confirmed that in the salt spray cabinet there was sufficient oxidizing capability (presumably from atmospheric oxygen) to generate hexavalent chromium [11]. In addition to these reasons, the constituents of treating-agent or the processing parameters also may influence the presence of hexavalent chromium as will be discussed below.

4. The effect of processing parameters and constituents of treating-agent

4.1. The effect of passivation processing parameters

The effect of processing parameters on the presence of hexavalent chromium is shown in Table 2. The formation rate of hexavalent chromium was retarded by lower working and baking temperatures. For example, the presence time of hexavalent chromium decreased from 20 d–6 d with the working temperature increasing from 20–35 °C. When the baking temperature increased from 60–150 °C, the presence time decreased from 20 d–10 d. The influence might be explained by the following two reasons. Generally speaking, the higher the temperature, the faster the reaction rate. Therefore, the higher working and baking temperatures could accelerate the oxidation rate of trivalent chromium and thus led to the much earlier formation of hexavalent chromium. Besides, the compact conversion coating was more likely to rupture under higher temperatures and generated a lot of micro-cracks, which resulted in the direct exposure to the air and hence accelerated formation rate of hexavalent chromium.

The shorter immersion time or the lower bath pH value also retarded the formation rate of hexavalent chromium. In general, the micro-cracks and thickness of trivalent chromium conversion coating first increase with the lengthening of immersion time or the rise of bath pH value, and thereafter decrease with further enhancement of immersion time or bath pH value [18]. In this study, the immersion time and bath pH values all equalled to or were less than the optimized processing parameters, which resulted in thicker conversion coating with more micro-cracks and hence accelerated formation of the hexavalent chromium. That is, thinner trivalent conversion coating with fewer cracks can be more resistant to the formation of hexavalent chromium.

4.2. The effect of treating-agent constituent

4.2.1. The effect of complexing agent

Complexion agent, such as organic acid, can chelate with trivalent chromate to form stable complexes, which accelerates the growth of conversion coating and improves corrosion resistance [19]. Meanwhile, complexing agent also may influence the formation of hexavalent chromium. Therefore, three trivalent iridescent treating-agents prepared by different complexing agents (oxalic acid, formic acid and acetic acid) were chosen for research. Fig. 2 presents the effect of different complexing agents on the hexavalent chromium formation. The appearance and corrosion resistance

Table 2
The effect of processing parameters on the presence of hexavalent chromium.

pH	Presence time (d)	Immersion time (s)	Presence time (d)	Working temperature (°C)	Presence time (d)	Baking temperature (°C)	Presence time (d)
1.3	25	15	22	20	20	60	20
1.6	20	20	18	25	15	80	16
1.9	15	25	15	30	10	100	15
2.2	9	30	8	35	6	150	10
2.5	7	35	3	40	3	180	4

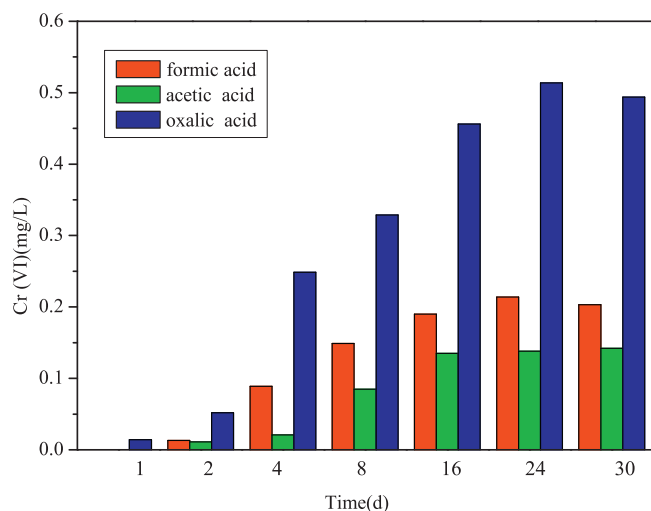


Fig. 2. The concentration of hexavalent chromium on trivalent chromium conversion coatings prepared by different complexing agents.

of fastener samples are shown in Table 3. It can be seen from Fig. 2 that the concentration of hexavalent chromium increased significantly with the prolonging of storage time. After 1 day, the concentrations of hexavalent chromium on the three conversion coatings were all quite low. Especially for the formic acid and acetic acid treating-agents, there was no hexavalent chromium detected on the conversion coating. Even for oxalic acid treating-agent, the concentration of hexavalent chromium was only 0.014 mg/L. However, after 4 days, the concentrations of hexavalent chromium formed on three conversion coatings increased significantly. Also, the growth of hexavalent chromium concentration on the conversion coating prepared by oxalic acid treating-agent was far greater than those by formic acid and acetic acid treating-agents. The concentration of hexavalent chromium on the oxalic acid conversion coating rapidly reached 0.49 mg/L after 30 days. Whereas, the hexavalent chromium production on acetic acid conversion coating

Table 3
The effect of different complexing agents on the appearance and corrosion resistance of conversion coating.

Complexing agent	Concentration (g/L)	Decorative performance	Corrosion resistance (h)
Formic acid	25	Pale white	48
	50	Pale white	48
	75	Pale green	60
Acetic acid	25	Pale white	48
	50	Pale white	72
	75	Yellow	48
Oxalic acid	25	Iridescent blue	96
	50	Iridescent blue	144
	75	Iridescent blue	168

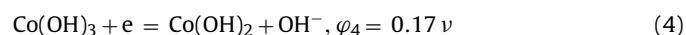
increased from the initial value of 0.011 mg/L to 0.14 mg/L after 24 days and then the value became nearly constant, so is the case with the formic acid conversion coating. For the exceptional result of the oxalic acid conversion coating, the higher concentration of hexavalent chromium may be associated with the more stable complex formed by oxalic acid and trivalent chromium. The detailed mechanism is still unclear and will be studied in detail in future research.

As discussed, compared to the complexing agent oxalic acid, formic acid or acetic acid could retard the presence of hexavalent chromium to an extent. However, the results in Table 3 indicate that the decorative performance and corrosion resistance of fastener samples prepared by the oxalic acid treating-agent were superior to those of the samples prepared by formic acid and acetic acid treating-agents. For example, a rather high corrosion protection was achieved (168 h to 3% white rust) at the 75 g/L oxalic acid. Also at 50 g/L oxalic acid, salt spray results (144 h 3% white rust) could be reached. However, even at the high concentration of formic acid (75 g/L) and acetic acid (75 g/L), only a temporary corrosion protection (48–72 h to 3% white rust) was achieved. Therefore, further development of treating-agent is necessary to satisfy both the requirements of higher corrosion resistance and less formation of hexavalent chromium. In order to evaluate the effect of other constituents on the hexavalent chromium formation, the oxalic acid treating-agent and the acetic acid treating-agent were chosen for further study.

4.2.2. The effect of bivalent cobalt

Cobalt is widely used to accelerate the reaction process and improve corrosion resistance. Hence, cobalt sulfate of different concentrations was added to the treating-agent. The presence of cobalt sulfate resulted in the production of more hexavalent chromium than when it is absent (Fig. 3). When 20 g/L cobalt sulfate was added, the concentration of hexavalent chromium on the oxalic acid conversion coating and the acetic acid conversion coating increased from 0.33–0.64 mg/L and 0.03–0.23 mg/L, respectively after 30 days. Also, it was found that the effect of cobalt sulfate on the hexavalent chromium on the oxalic acid conversion coating was more significant. For example, in the presence of 20 g/L cobalt sulfate, the concentration of hexavalent chromium on oxalic acid conversion coating increased to 0.43 mg/L after 8 days, while the concentration of hexavalent chromium on acetic acid conversion coating increased to only 0.13 mg/L.

The enhancement may be explained by oxidation and the catalytic properties of cobalt. On one hand, under certain conditions, such as appropriate humidity and temperature, bivalent cobalt is oxidized to trivalent cobalt [13].



It can be seen that the potential of Eq. (4) ($\varphi_4^0 = 0.17 \nu$) is lower than that of Reaction (3) ($\varphi_3^0 = 0.403 \nu$), which indicates that bivalent cobalt may be oxidized to trivalent cobalt. Trivalent cobalt is not stable in that it can grab the electrons from trivalent chromium whereby trivalent chromium is oxidized to hexavalent chromium. On the other hand, it may act as the catalyst to promote

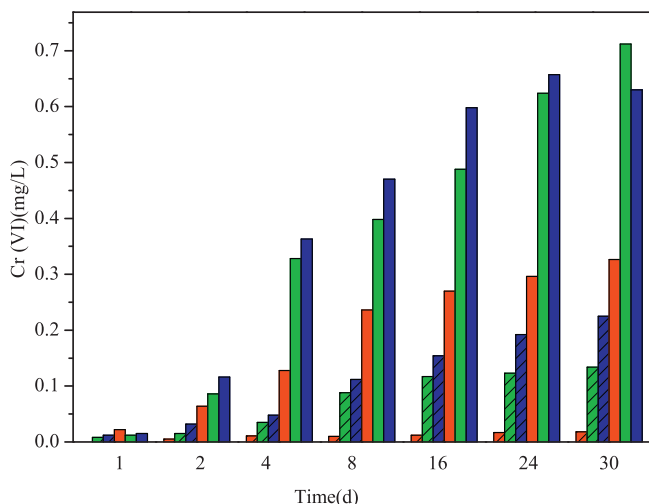


Fig. 3. Effect of bivalent cobalt at different concentrations (red: cobalt sulfate = 0 g/L, green: cobalt sulfate = 10 g/L, blue: cobalt sulfate = 20 g/L) on the concentration of hexavalent chromium on the acetic acid conversion coating (dense pattern) and the oxalic acid conversion coating (no pattern). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the oxidation reaction and hence accelerates the formation rate of hexavalent chromium.

4.2.3. The effect of nitrate anion

Sodium nitrate is an essential constituent that can increase the interface reaction, which oxidizes Zn to Zn²⁺ to form the uniform and compact conversion coating. The experiments were conducted under the same conditions, except that cobalt sulfate was replaced by sodium nitrate. The results are presented in Fig. 4. It can be seen that the effect of sodium nitrate on the presence of hexavalent chromium on acetic acid conversion coating was slight. The concentration of hexavalent chromium was at first about 0.15 mg/L in the absence of sodium nitrate after 8 days and only increased to 0.18 mg/L when 200 mg/L of sodium nitrate was added. The similar trend was observed for longer storage time and higher concentration of sodium nitrate. After 30 days, the concentration of hexavalent chromium also only increased to 0.20 mg/L with the

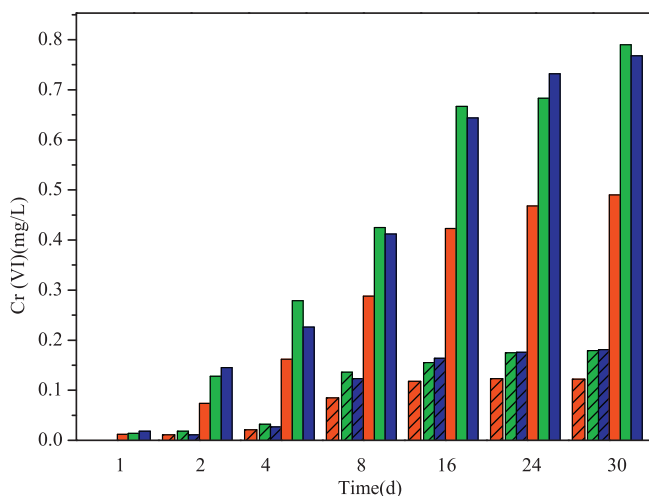


Fig. 4. Effect of sodium nitrate at different concentrations (red: sodium nitrate = 0 g/L, green: sodium nitrate = 200 g/L, blue: sodium nitrate = 400 g/L) on the concentration of hexavalent chromium on the acetic acid conversion coating (dense pattern) and the oxalic acid conversion coating (no pattern). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

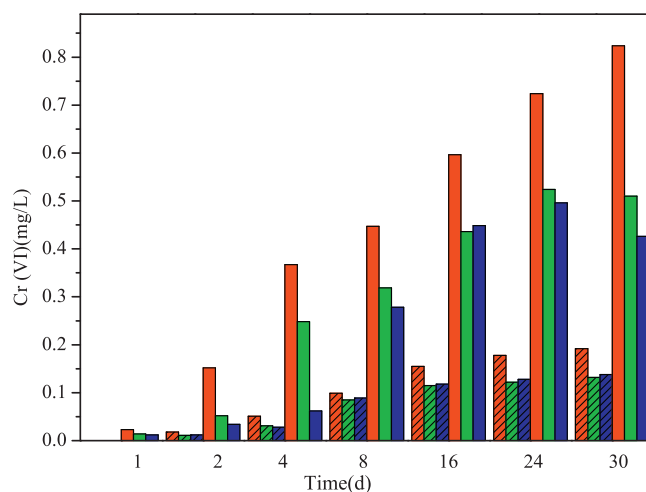


Fig. 5. Effect of D-gluconic acid at different concentrations (red: D-gluconic acid = 0 g/L, green: D-gluconic acid = 50 g/L, blue: D-gluconic acid = 100 g/L) on the concentration of hexavalent chromium on the acetic acid conversion coating (dense pattern) and the oxalic acid conversion coating (no pattern). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

addition of 400 mg/L sodium nitrate. However, the presence of sodium nitrate markedly increased the concentration of hexavalent chromium on the oxalic acid conversion coating even at the early stage. When 200 g/L sodium nitrate was added, the concentration of hexavalent chromium increased to 0.43 mg/L fairly rapidly after 8 days and was then added up to 0.79 mg/L after 30 days.

The increase of hexavalent chromium in the presence of nitrate anion can be explained by considering the consequent reaction under alkaline conditions [13]:



Nitrate anion is an effective oxidant agent especially under alkaline conditions. Compared to the reduction potential of Reactions (1) and (2) ($\varphi^0 = -0.12\text{v}$), the higher reduction potential of Reaction (5) ($\varphi_5^0 = 0.01\text{v}$) indicates that the trivalent chromium is oxidized to hexavalent chromium more easily in the presence of nitrate anion.

4.2.4. The effect of D-gluconic acid

The effect of the hydroxyl compound D-gluconic acid with different concentrations on the hexavalent chromium formation was tested (Fig. 5). It is obvious that the addition of D-gluconic acid could inhibit the hexavalent chromium formation to some extent. At the early stage, the concentration of hexavalent chromium on the two conversion coatings went through a slight growth. However, with the increase of storage time, the concentration of hexavalent chromium on the two conversion coatings decreased due to the addition of D-gluconic acid. The inhibition effect was more distinct in the formation of hexavalent chromium on the oxalic acid conversion coating: After 30 days, the concentration of hexavalent chromium (0.50 mg/L) in the presence of 50 g/L D-gluconic acid was lower than when in the absence of D-gluconic acid (0.82 mg/L). However, the concentration of hexavalent chromium on the acetic acid conversion coating decreased slightly. After the same storage time (30 days), the reduction of concentration of hexavalent chromium was only 0.04 mg/L. The possible reason for the lower hexavalent chromium may be associated with the formation of compactly protective film covered on trivalent chromium conversion coating. The compact film could protect the trivalent chromium conversion coating from exposure to the air outside and thus significantly reduce the oxidation rate of trivalent chromium.

5. Conclusions and suggestions

This paper reported the effects of processing parameters and constituents of treating-agent on the presence of hazardous hexavalent chromium on trivalent chromium conversion coating. The results demonstrated that the presence of trace hexavalent chromium on trivalent chromium conversion coating might be explained by considering the following three factors. Firstly, due to the exposure to the air, the samples can be oxidized by oxygen in the presence of water, which resulted in the presence of trace hexavalent chromium. Secondly, longer immersion time, higher bath pH value and higher working and baking temperatures can accelerate the formation rate of hexavalent chromium. Finally, certain constituents of the treating-agent can also act as catalysts or oxidant agent to accelerate the formation of hexavalent chromium. Most importantly, the addition of hydroxyl compound D-gluconic acid can reduce the risk of the formation of hexavalent chromium on trivalent chromium conversion coating. Therefore, the formation rate of hexavalent chromium can be greatly reduced via the optimization of processing parameters and constituents of treating-agent.

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References

- [1] A. Amita, T. Vinod, B. Purnendu, Extent of oxidation of Cr (III) to Cr (VI) under various conditions pertaining to natural environment, *J. Hazard. Mater.* 128 (2006) 164–174.
- [2] P. Robert-sainte, M.C. Gromaire, B. Degouvello, M. Saad, Annual metallic flows in roof runoff from different materials: test-bed scale in Paris conurbation, *Environ. Sci. Technol.* 43 (2009) 5612–5618.
- [3] D. Lindström, I.O. Wallinder, Long-term use of galvanized steel in external applications. Aspects of patina formation, zinc runoff, barrier properties of surface treatments, and coatings and environmental fate, *Environ. Monit. Assess* 173 (2011) 139–153.
- [4] D. Lindström, Y. Hedberg, I.O. Wallinder, Chromium(III) and chromium(VI) surface treated galvanized steel for outdoor constructions: environmental aspects, *Environ. Sci. Technol.* 44 (2010) 4322–4327.
- [5] N. Panichev, W. Mabasa, P. Ngobein, K. Mandiwana, S. Panicheva, The oxidation of Cr (III) to Cr (VI) in the environment by atmospheric oxygen during the bush fires, *J. Hazard. Mater.* 128 (2006) 937–941.
- [6] International Agency for Research on Cancer (IARC), IARC Monographs of the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Chromium, Nickel and Welding, IARC, Lyon, 1990.
- [7] 2002/95/EC, The Restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) [Z], 2003:L37/21.
- [8] M. Ruhland, B. Casey, Part finishing and the new RoHS and ELV directives: with compliance of popular finishes often in question, manufacturers should re-examine their options and prepare for change, *Met. Finish.* 104 (2006) 68–72.
- [9] P. Wyen, The end of life vehicle directive and international material data system, *Prod. Finish.* 5 (2005) 58–63.
- [10] F. Defloriana, S. Rossia, L. Fedrizzib, P.L. Bonoraa, EIS study of organic coating on zinc surface pretreated with environmentally friendly products, *Prog. Org. Coat.* 52 (2005) 271–279.
- [11] T. Rochester, Z.W. Kennedy, Unexpected results from corrosion testing of trivalent passivates, *Plat. Surf. Finish.* 94 (2007) 14–18.
- [12] Z.K. Kennedy, T. Rochester, D. Wichern, T. Kelly, T. Mooney, B. Terry, P. George, E. Olander, S. Ramajayam, Please explain theory of trivalent passivation. <http://www.finishing.com/470/49.shtml>.
- [13] Z.W. Kennedy, Behavior of trivalent passivates in accelerated corrosion tests, *Electroplat. Finish.* 27 (2009) 23.
- [14] J. Xiong, Reasons for the production of hexavalent chromium in trivalent passivation coating, *Electroplat. Finish. (China)* 27 (2008) 23–24.
- [15] People's Republic of China Electronic Industry Standard, Test method for hazardous substances in electronic information product, SJ/T 11365-2006. 2006, 11.
- [16] International Electrotechnical Commission, Procedures for the Determination of Levels of Six Regulated Substances (Lead, Mercury, cadmium, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Diphenyl Ethers) in Electrotechnical Products[S], IEC62321 ed.1 111/54/cdv. 43–46, 2006, 5.
- [17] ASTM B 117-2009, Standard Practice for Operating Salt Spray (Fog) Apparatus, American.
- [18] K.W. Cho, V.S. Rao, H.S. Kwon, Microstructure and electrochemical characterization of trivalent chromium based conversion coating on zinc, *Electrochim. Acta* 52 (2007) 4449–4456.
- [19] O.D. Lewis, D. Greenfield, R. Akid, R.H. Dahm, G.D. Wilcox, Investigation into use of simple molybdate passivation treatments on electrodeposited zinc coatings, *Trans. Inst. Met. Finish.* 8 (2006) 188–195.