P. POKORNY, P. TEJ, P. SZELAG

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CHROMATE CONVERSION COATINGS AND THEIR CURRENT APPLICATION

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This paper describes formation, composition and possible production technologies of application chromate coatings. Summation of common examples of applications of these coatings in corrosion protection of metals and alloys is provided. Individual chromate coatings are divided by their dominant anions either with Cr^{VI} or Cr^{III}. Restrictions of chromate coatings with dominantly Cr^{VI} and related toxicity of hexavalent chromium is discussed in detail. In conclusion, examples of both chromium and other, alternative coatings are summed up. Application of these coatings as a protection for concrete hot-dip galvanized reinforcement is also reviewed.

Key words: chromate coatings, conversion coatings, aluminium alloys, toxicity, hot – dip galvanized reinforcement

INTRODUCTION

Metal and alloy coating is one of the most common means of protection against corrosion. Coatings also provide other properties, such as mechanical, physical and also esthetic.

Commonly used coatings are inorganic non-metal coatings. These can be divided to so-called contact and conversion coating group. Contact coatings are for example enamel, cement and ceramic coatings. These coatings are applicable on any metal or alloy, regardless of the manufacture procedure, their composition and inherent thickness; these coatings are non-selective [1].

On the other hand, conversion coatings are selective. The reason for this is the fact that the coating is formed by reaction between ions in the deposition bath and metal cations dispersed to the bath during the initial corrosion reaction between the bath and coated metal [1,2].

Although the application of these coatings in industry is limited compared to the last century, this surface treatment is still more popular than coating by organic compounds.

After steel phosphating or aluminium anodizing (eloxing), chromate process is the most common conversion surface treatment (Figure 1). Chromate coatings serve as additional corrosion protection layer predominantly used on electrodeposited zinc and cadmium coatings. These coatings are also used for protection and for aesthetic reasons as a final surface layer on zinc castings, moldings and semi-finished magnesium products and its alloys as well as on copper and its alloys. They are often used as interlayer providing adhesive surface for both conventional and powder paints. It can be alternatively used as absorbent layer for lubricant, however phosphate layers produce better results [2, 3].

Chromate layers are deposited on coated surface rather by dipping than spraying. In lines for coating of galvanized or aluminum foils passivation is realized by specific technology – coil coating.

Other conversion coatings are only marginally important in current industry. Oxalate and böhmite coatings were replaced in the past (with few exceptions) by other surface treatment technologies.

Although the chromate coatings provide superior properties either from corrosion protection and aesthetic point of view, their use in the EU is limited. The reason is the carcinogenic component of the working bath - Cr^{VI} [2]. New kinds of working baths with trivalent chromium have been thus introduced – the term “chromium (VI)-free passivation” to highlight the difference compared to the classical passivation baths.

History

The introduction of chromate coating technology into practice cannot be precisely dated. It is presumed that they were introduced concurrently with the development of aerospace industry, i.e. beginning of the 20th

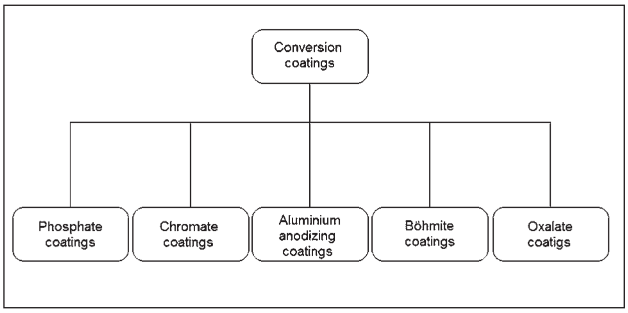

Figure 1 Classification of conversion coatings [1]

P. Pokorny, P. Tej – Czech Technical University – Klokner Institute, Prague, Czech Republic
P. Szelag – Pragochema Prague, Prague, Czech Republic

century, when means how to protect aluminium and its new alloys – duraluminums, were investigated.

The original baths composed of alkaline metal carbonates and dichromates. Coated components were immersed in these baths for several hours at temperature 90 – 95 °C. Since 1940s, the efficiency of acidic baths (pH < 1,8) with chromates, dihydrogen phosphates and fluorides was investigated. The temperature of these baths was maintained at 25 – 30 °C and the immersion time was only 2 – 5 minutes. Modern working baths are based on these acidic baths with addition of other anions (fluorides, phosphates, ferricyanides etc.) to speed up the formation of coating [2].

Coating characterization and mechanism of its formation

Chromate coatings on metal surface are formed via oxidation – reduction processes and they comprise of very complex mixture of zinc hydroxide, hydrated alkaline zinc chromates, alkaline chromium chromate and chromium hydroxide. These compounds are formed by interactions between cations of base metal produced by anodic corrosion reaction with chromate, resp. chromite ions (also chromium hydroxide) formed by hydrogen reduction. Hydrogen is produced in the cathodic corrosion reaction [2, 4].

Deposition chromate baths are acidic (pH <1,8) with sulfuric acid, chromates, dihydrogen phosphates, fluorides and complex anions to support the formation of coating. Composition of the bath is adjusted depending on the coated metal (conventional chromate coating Cr^{VI} on hot – dip galvanized surface – see Figure 2).

Exact mechanism of coating formation process is not known. Chromate layer creation presumably consists of three stages:

1. Zinc dissolution
   $Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$
   $Zn \rightarrow Zn^{2+} + 2\,e^-$
2. Hexavalent chromium reduction
   $H_2CrO_4 + 3/2\,H_2 \rightarrow \underline{Cr(OH)_3} + H_2O$
   $HCrO_4^- + 7\,H^+ + 3\,e^- \rightarrow Cr^{3+} + 4\,H_2O$
3. Layer formation
   $Zn^{2+} + 2\,OH^- \rightarrow \underline{Zn(OH)_2}$
   $2\,Zn^{2+} + HCrO_4^- + 2\,H_2O \rightarrow \underline{ZnCrO_4Zn(OH)_2} + 3\,H^+$
   $Cr(OH)_3 + H_2CrO_4 \rightarrow \underline{Cr(OH)CrO_4} + 2\,H_2O$

The reactions in the chromium (VI)-free baths with only trivalent chromium are similar, skipping the reduction of Cr^{VI} (for example see Figure 3).

1. Zinc dissolution
   $Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$
   $Zn \rightarrow Zn^{2+} + 2\,e^-$
2. Layer formation
   $Zn^{2+} + 2\,OH^- \rightarrow \underline{Zn(OH)_2}$
   $Cr^{3+} + 3\,OH^- \rightarrow \underline{Cr(OH)_3}$

3 $Zn^{2+} + Cr^{3+} + 9\,OH^- \rightarrow \underline{Cr(OH)_3.3\,Zn(OH)_2}$

4 $Zn^{2+} + 6\,OH^- + 2\,F^- \rightarrow \underline{ZnF_2.3\,Zn(OH)_2}$

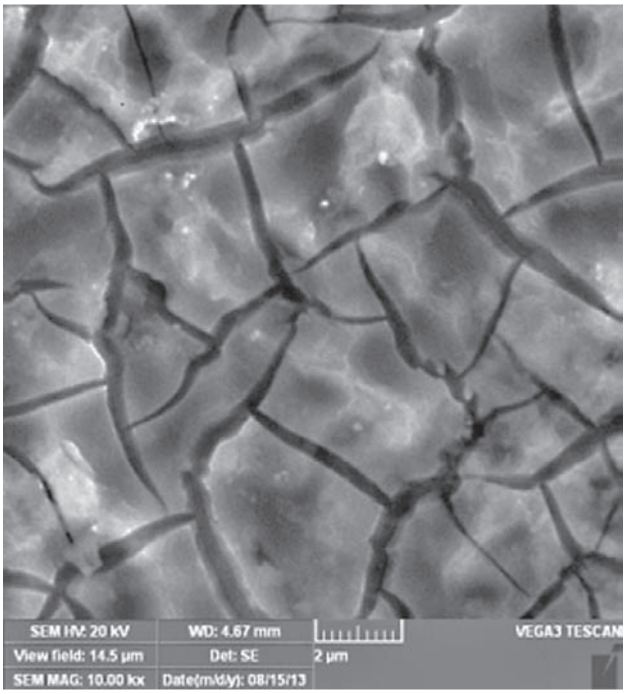

Figure 2 Chromate (Cr^{VI}) coating on hot – dip galvanized steel [2]

Chromate process produces iridescent amorphous gel-like coating with typical thickness of 150-350 nm. The trivalent chromium gives the coating enhanced strength and hardness. Hexavalent chromium improves the corrosion resistance by inhibiting the corrosion reaction and also provides it with so-called self-healing capability.

The coating is, thanks to the partial mobility of chromate anions in gel layer, able to maintain its integrity even in the case of being mechanically damaged. Based on the ratio between hydrated zinc chromates, chromium, other metals and thickness of produced layer, different chromate coatings are characterized. In practice, coatings are differentiated based on their color. From this point of view, color of chromate layers ranges from pure transparent to rainbow-like yellow or brass, brown to olive green or black. Generally - the darker hue of the coating means better corrosion resistance, but also higher Cr^{VI} concentration [2, 4, 5].

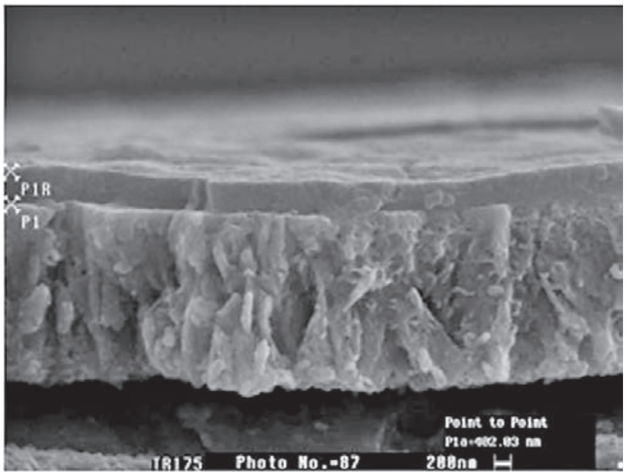

Figure 3 Cross – section through a latest generation Cr^{III} film on zinc [6]

Technology of production chromate coating with only trivalent chromium was developed as environmentally acceptable hexavalent chromate coating replacement for predominantly final surface treatment of electrodeposited zinc treatment. Trivalent chromium compounds are non-toxic and pose no health or ecological risk. Such coatings are transparent to blue-like, provide substantially lower corrosion resistance compared to the Cr^{VI} based coatings and are not capable of self-healing [2,4,7].

Toxicity

It has been stated above that use of chromate coatings is strongly limited by regulatory authorities. The reason for this is proven carcinogenicity, mutagenicity and toxicity for reproduction (category 1B in all cases) of chromium (VI) compounds. Moreover, it has been proven that hexavalent chromium species are dissolved in/by the human perspiration [2, 4].

Carcinogenic impact of Cr^{VI} on human lungs is verified, however exact mechanism of its attack on DNA molecule has not yet been confirmed. It is presumed that individual Cr^{VI} and/or Cr^{III} species are not harmful, however in the presence of biological reducing agents (ascorbate, gluthatione, L-cystein etc.), the Cr^{VI} reacts forming metastable reactive Cr^{V}/Cr^{IV} species or other compounds capable of damaging the DNA molecule. Harmlessness of Cr^{VI} without biological reducing agents has been proven in the past. The other possible mechanism of toxicity is being discussed – perocomplexes with Cr^{VI} are very reactive and passable through the cell membrane. Moreover, it is being proven that the highly-reactive Cr^{V} compounds can be stabilized in human body by common α – hydroxycarboxyle acid group. The •OH radicals forming during oxidation of Cr^{III}, Cr^{IV}, Cr^{V} by hydrogen peroxide also have some impact [8 - 10].

By the Commission Regulation (EU) No 348/2013 from 4/17/2013, affecting the appendix XIV of the regulation of European Parliament and Council (ES) number 1907/2006 about registration, evaluation, authorization and limitation of chemical substances, production of inorganic compounds with Cr^{VI} (chromium trioxide, acids derived from this oxide, their oligomers, potassium dichromate, ammonium dichromate and others) is required to be authorized by European Chemical Agency; this authorization is charged. Without this authorization/registration, further production of these compounds will be, after certain date, considered illegal.

These legislative changes are aimed at limitation the production of these compounds and to support exploration of other, ecological alternatives [2].

Current application of chromate coatings

Due to the proven ecotoxicity and carcinogenity, the use of Cr^{VI} is being reduced primarily in the automotive industry. Before 2007, the Directives set the limit of hexavalent chromium to maximum of 2 g per the whole vehicle (up to 3,5 t). Since the amount cannot be exactly measured in the industrial production, this surface treatment has been replaced by other surface pre-treatments. The chromate was originally used for pretreatment of e.g.: wheel rims, roof racks and zinc plated parts of fasteners. In these applications, the coatings based on Zr^{IV} are currently used [11].

In electrical engineering, the chromate layers with predominantly Cr^{VI} were used. The goal was to enhance the corrosion resistance of zinc plated fasteners and cases. Other application of chromate coating was for enhance of the corrosion resistance of components sensitive to reductions of conductivity due to corrosion. Currently, chromate coatings are used in neither one of these.

In the European automotive and electrical engineering industry, replacement of classical chromate process by chromium (VI)-free has been finished.

Conversely, the Cr^{VI} chromate process is maintained in full scale in aerospace and military industry. In aerospace industry, the external parts of plane hull are chromate. Other applications in the industry include anticorrosion treatment for parts with electrodeposited zinc, cadmium or eventually ZnNi coating, often coated with organic coating. Specific chromate parts are for example individual parts of some aircrafts (inner and outer valve of the main shock absorber, side and torsion struts etc.). Overall, about 80 % of landing gear is treated in this manner. Flight control system also employs chromate parts – steel hinges, various parts of the rudder system, wing parts, i.e. in this case outer trailing edge flaps. In some cases, both aerospace and military industry employs Cr^{III} chromate coatings, in particular for interior hull parts.

Hot-dip zinc galvanized concrete reinforcement chromate coating

The chromate coating layers were considered in the construction industry as suitable final surface treatment of hot-dip zinc galvanized concrete reinforcement. In fresh cement paste (pH ~ 13,0 – 13,5), the zinc coating corrodes actively while producing hydrogen which enters still plastic cement paste. Due to this phenomenon, the porosity on the interface is increased and the cohesion is thus decreased. This can be prevented using compact chromate coating [12].

In his work, Kouřil [13] studied additional protection of zinc plated steel by means of chromate coating in case of exposition of the steel in alkaline environment modeling the concrete pore solution. Efficiency of protection of chromate layer based on either Cr^{III} or Cr^{VI} depends on the pH of the alkaline solution. In model pore solution of pH 12,5, corrosion resistance of zinc plated samples coated by any of the two coatings was increased. However, at pH of 13,5, high corrosion rates were measured on the sample protected by coating based predominantly on Cr^{III} compounds. The corrosion rate of sample coated by predominantly Cr^{VI} compounds in this solution without chlorides was ca tenths of µm per year, which is, as author noted, one order of magnitude less than commercial zinc plated steel without surface treatment. Other works on the topic agree that the Cr^{VI} coating is able to prevent active corrosion of zinc in fresh concrete.

Alternative coatings

At present, alternative coatings providing comparable corrosion resistance to chromate coatings are researched. The coatings based on Zr^{IV} and Ti^{IV} showed some success. Produced layers contain hydrated titanium and zirconium oxides and hydroxides but do not reach the thickness of common chromate coating, the working baths are more expensive and the pre-coating surface treatment is more complicated. Their application in industry is only marginal. Worth mentioning as well are currently investigated coatings and inhibition systems based on $Ce^{III/IV}$ or $La^{III/IV}$, or eventually other lanthanoids. Their effect is probably comparable to the coatings prepared from the baths with active titanium and zirconium, however they are disproportionally more expensive [2, 4].

CONCLUSION

Chromate coatings based on Cr^{VI} are still a popular surface treatment method mostly for their unmatched corrosion resistance mainly on components coated electrocoated by zinc or cadmium, or on aluminum and aluminum alloy products. Alternative coatings with non-verified negative impact on human health and without ecotoxicity (based on Cr^{III}, Zr^{IV}, Ti^{IV}, $Ce^{III/IV}$, $La^{III/IV}$ etc.) cannot provide comparable corrosion protection.

Due to the proven carcinogenicity and ecotoxicity, the Cr^{VI} chromate process in automobile industry was replaced by other coatings, commonly based on Zr^{IV}. Chromate coatings are no longer used in electrical engineering industry. It is still employed in military and aerospace industry for aluminum alloys, zinc or cadmium-coated components intended for final organic coating.

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Note: The responsible translator for the English language is
K. Štětková, CTU – Klokner Institute, Prague, Czech Republic