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Cobalt-Free Zinc and Zinc-Alloy Passivation

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ABSTRACT

This article will detail an alternative to cobalt-containing trivalent chromium passivation. Field results from this unique passivate system have demonstrated comparable corrosion protection to existing cobalt-containing Cr(III)-based passivates. The new system is easy to handle and offers a broad operation range. The performance, appearance and passivation mechanism, as well as some limitations, will be discussed.

Keywords: Cobalt-free passivates, hexavalent Cr substitutes, trivalent Cr passivates, REACh compliance

Introduction

Twenty years ago, using chromate conversion coatings to protect zinc and zinc-alloy deposits was considered state-of-the-art. Due to severe health and environmental (HS&E) concerns, the use of hexavalent chromium [Cr(VI)] was virtually banned,[1] resulting in the acceptance and use of more environmentally-friendly, trivalent chromium [Cr(III)]-based passivates as a viable option.

However, these environmentally-friendly passivates have now come under HS&E pressure as well, due to the small amounts of cobalt salts required to assist in film formation.[2] In Europe, most cobalt salts are already on a proposal list for banning (SVHC - Substance of Very High Concern)[3] - proposal list.). Therefore, a new generation of passivate systems for zinc and zinc alloy applications is required.

This article will detail an alternative to cobalt-containing trivalent chromium passivation. Field results from this unique passivate system have demonstrated comparable corrosion protection to existing cobalt-containing Cr(III)-based passivation. The new system is easy to handle and offers a broad operation range. The performance, appearance and passivation mechanism, as well as some limitations, will be discussed.

REACh / SVHC as a driving force

"REACh" is the regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals. It entered into force on June 1, 2007. It streamlines and improves the former legislative framework on chemicals of the European Union (EU). The main aims of REACh are to ensure a high level of protection of human health and the environment from the risks that can be posed by chemicals, the promotion of alternative test methods, the free circulation of substances on the internal market and the enhancement of competitiveness and innovation. REACh makes industry responsible for assessing and managing the risks posed by chemicals and providing appropriate safety information to their users. In parallel, the European Union can take additional measures on highly dangerous substances, where there is a need for complementing action at EU level."[4]

As a result of REACh, the production and use of chemicals is regulated. Substances that are produced and/or used in amounts of more than 1000 kg/year must be registered and a risk assessment must be performed. In addition to the REACh regulation, substances with high risks will be listed on the SVHC list. Once a substance has entered the list, the applicants and producer must demonstrate that the socioeconomic benefit of using this substance is higher than the risk of using it. The goal is obvious: make a socioeconomic analysis, check which process is the "best" concerning REACh and avoid substances of risk if possible.

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If it is necessary to use substances of concern, this must be reported to ECHA (European Chemical Agency) and a request made for the document that approves their usage. The applicants must show excellent reasons to obtain usage approval for a given time.

SVHC and passivates for zinc and zinc alloys

The SVHC candidate list already contains some prominent members of the class "Corrosion Protection Chemicals for Zinc," such as hexavalent chromium compounds and cobalt salts. For these substances a dossier has been collected and published. Table 1 summarizes the substances that are under investigation which may affect the plating industry.

Table 1 - SVHC candidate list: Substances that are under investigation extracted for the plating industry. Yellow background denotes typical substances that may be used for the corrosion protection of zinc and zinc alloys.[3]

Name	Reason for inclusion
Boric acid	Toxic for reproduction (Article 57c).
Disodium Tetraborate, anhydrous	Toxic for reproduction (Article 57c).
Tetraboron disodium heptaoxide, hydrate	Toxic for reproduction (Article 57c).
Potassium dichromate	Carcinogenic, mutagenic and toxic for reproduction (Articles 57a,b and c).
Ammonium dichromate	Carcinogenic, mutagenic and toxic for reproduction (Articles 57a,b and c).
Potassium chromate	Carcinogenic and mutagenic (Articles 57b and c).
Sodium chromate	Carcinogenic, mutagenic and toxic for reproduction (Articles 57a,b and c).
Cobalt dichloride	Carcinogenic (Article 57a).
Sodium dichromate	Carcinogenic, mutagenic and toxic for reproduction (Articles 57a,b and c).
Cobalt(II) sulfate	Carcinogenic and toxic for reproduction (Articles 57a and c).
Cobalt(II) dinitrate	Carcinogenic and toxic for reproduction (Articles 57a and c).
Cobalt(II) carbonate	Carcinogenic and toxic for reproduction (Articles 57a and c).
Cobalt(II) diacetate	Carcinogenic and toxic for reproduction (Articles 57a and c).
Chromium trioxide	Carcinogenic and mutagenic (Articles 57b and c).
Chromic acid, dichromic acid and oligomers of chromic acid and dichromic acid	Carcinogenic (Article 57a).

In the case of Cr(VI) compounds, the risks have been widely discussed in the past. However, despite cobalt being contained in vitamins (*e.g.*, vitamin B12), cobalt salts are now under pressure as well. According to reports, cobalt salts have been identified as CMR (carcinogenic, mutagenic and reproductive toxic).[5] The consequence of this is that shortly, cobalt salts will be banned.[6,7]

Although the SVHC list is not active, it already has an impact. Sodium chromates are no longer commercially available in the EU as the registration fees are higher than the expected benefit for the producer. The production of sodium chromate has therefore been terminated. This may well become the fate of other CMRs as well.

New Cr(VI)- and cobalt-free passivates for zinc and zinc alloys

The risk of a ban on cobalt salts has required the development of a new generation of zinc and zinc alloy passivates without CMRs, SVHCs, etc. Therefore, a new passivation solution was developed that does not contain cobalt OR contain OR generate Cr(VI). Additionally, the system offers similar corrosion protection to cobalt-containing passivates, has an attractive appearance and works on zinc alloys as well.

The newly developed passivate system consists of a Cr(III)-based multi-core complex that compliments the (100) crystal orientation of a zinc deposit. On contact with the zinc surface, Cr(II) is generated as an intermediate that forms an oligomeric 200-300 nm film on the zinc surface. The resulting finish is iridescent to bluish/yellow in color (Fig. 1).

Figure 1 - Cobalt-free passivated zinc plated parts.

Some properties and parameters are shown in Table 2 together with the cobalt-containing thick film passivate data as a benchmark.

As can be seen from Table 2, the properties and application parameters of the new system are quite similar to those of the traditional cobalt-containing processes. The main parameters for functionality are immersion time and bath temperature. Longer dipping times, higher temperatures and higher concentrations of the complex in the process bath lead to better corrosion resistance. The pH and temperature mainly influence the appearance. The lower the temperature the more bluish the passivate becomes. On zinc-iron alloys a bright stainless steel-like finish is obtained.

Surprisingly, the new passivate leads to a higher gloss and less “black spot corrosion” compared to the “old passivates.” Figure 2 shows a direct comparison. The cobalt-free parts on the left side are much brighter and show fewer black spots after NSS.

Some further areas of development have been identified, including their functionality:

- Over poor quality zinc deposits
- Over zinc plated cast iron
- At rack contact points
- In the case of severe scratches

Cobalt-free passivate over poor quality zinc deposits

In benchmarking experiments, it was observed that the cobalt-free passivate showed excellent performance over technical bright surfaces that are generated by typical acid or alkaline zinc plating processes. However, if for example, the carrier or brightener were significantly below the optimums, then the corrosion resistance was reduced dramatically. The explanation for this behavior is related to the film building mechanism. The cobalt-free passivate generates a very homogeneous film on the (100) crystal orientation.[8,9] If the (101) orientation is dominant, the film becomes less homogeneous and the corrosion resistance is reduced (Fig. 3).

The (100) [or (010) or (001)] orientation is parallel or perpendicular to the surface. This allows a homogeneous surface reaction with the passivate complex (Fig. 4).

In the case of a (101) orientation the “attack” of the passivate on the zinc surface occurs at an angle. This produces a passivate film with more defects and significantly different thicknesses.

Table 2 - New cobalt-free versus state-of-the-art thick film passivate.

Property	Parameter	Co-free passivate	Co-containing thick film passivate
Corrosion protection	NSS (ASTM B117, DIN EN ISO 9227) **White rust**	Barrel > 250 hr Rack > 500 hr	Barrel > 300 hr Rack > 550 hr
	NSS (ASTM B117, DIN EN ISO 9227) **Red rust**	Barrel > 700 hr Rack > 700 hr	Barrel > 700 hr Rack > 700 hr
	NSS (ASTM B117, DIN EN ISO 9227) **with Sealant; White Rust**	Barrel > 300 hr (ZnFe > 400 hr Rack > 600 hr	Barrel > 300 hr Rack > 600 hr
	Black spot corrosion (NSS)	Fewer black spots compared with Co-containing passivates	Black spots
Appearance	On acid zinc	Bluish/yellowish to iridescent	Bluish/yellowish to iridescent
	On alkaline zinc	Bluish to iridescent	Bluish to iridescent
	Brightness	Improved brightness	Slightly cloudy; stains
Application parameter	Working temperature	35-60°C (95-140°F)	30-60°C (86-140°F)
	pH range	1.8-2.2	1.8-2.2
	Time in solution	30-120 sec	30-120 sec
	Zn(II) tolerance	>15 g/L	Up to 15 g/L
	Fe(II)/Fe(III) tolerance	100 ppm	100 ppm
	Ion exchange technology applicable (for Fe Removal)	Yes	Yes
	Masking agent for iron available	Available	Available
Compatibility	Paint adhesion	Good	Poor
	Wax-based seal	Good	Good
	Acrylic-based seal	Good	Good
	Inorganic seal	Excellent	Excellent
Legislation	SVHC candidate list	Clear	Contains Co salts (CMR)
	REACh	Clear	Clear (until SVHC becomes active)
	SIN	Clear	Clear
	TSCA	Listed	Listed
	China toxic list	Clear	Clear

Figure 2 - (L) Fasteners with cobalt-free passivate; (R) fasteners with cobalt-containing passivate (both after 240 hr NSS).

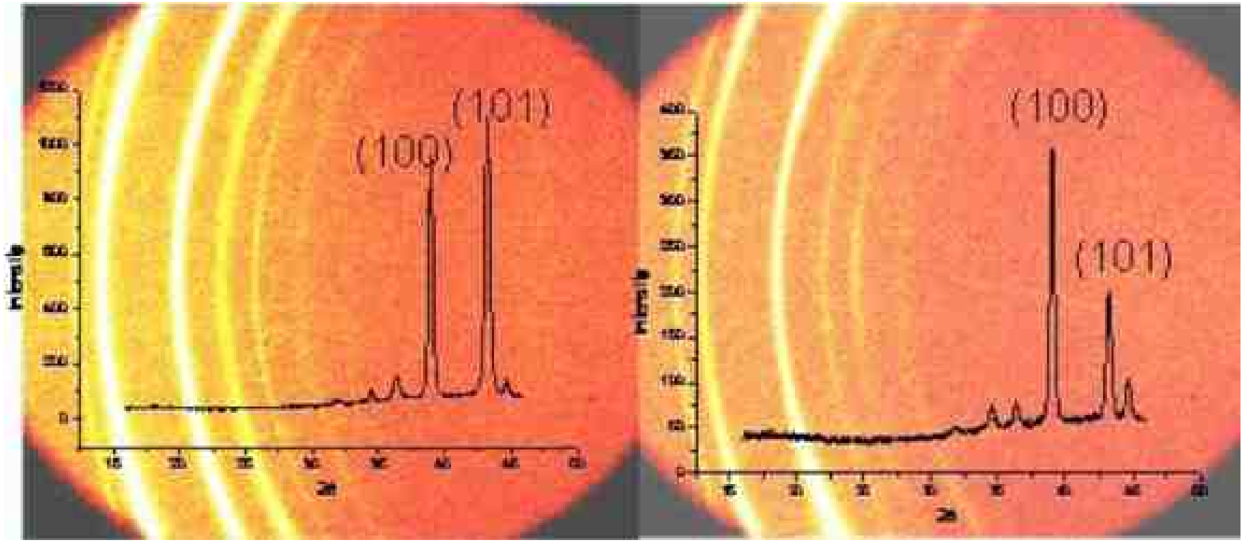

Figure 3 - Crystal orientation: the larger the ratio of (100) to (101), the better the corrosion protection.

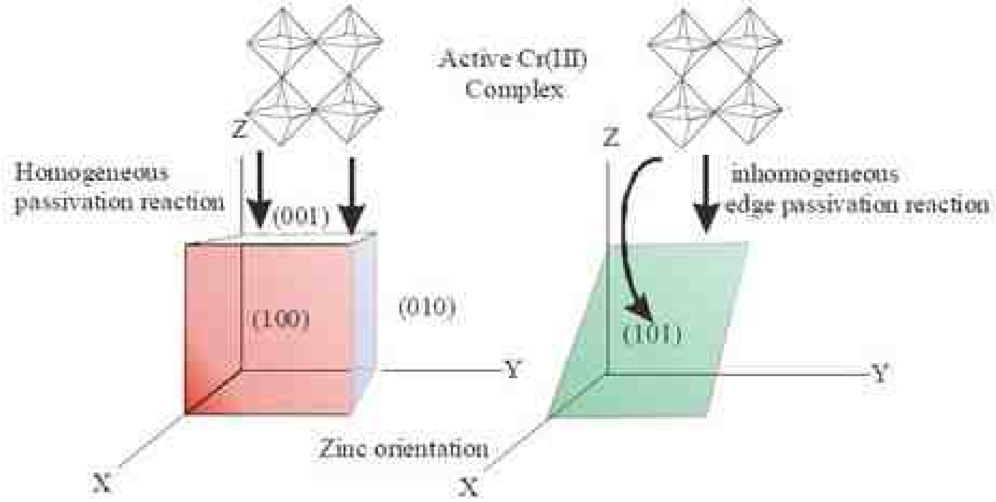

Figure 4 - Homogeneous passivation reaction with (L) (100) crystal orientation and (R) non-homogeneous passivation reaction with (101).

Zinc-plated cast iron, severe scratches and contact points

The cobalt-free passivate showed reduced performance under defect conditions (*e.g.*, poor substrates, scratches or contact points). The principle question here is: Why do the cobalt-containing passivates perform better than the cobalt free? A plating and corrosion experiment demonstrates the difference. On the right side of Fig. 5, a cap is shown which is passivated with the new cobalt-free system. On the left side, a passivate with 1.0 g/L cobalt is applied.

A SEM surface analysis shows the differences. SEM photos were taken of the deliberately introduced defects and are shown in Fig. 6.

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Figure 5 - Caps after 240 hr NSS: (L) cobalt-containing passivate; (R) cobalt-free passivate.

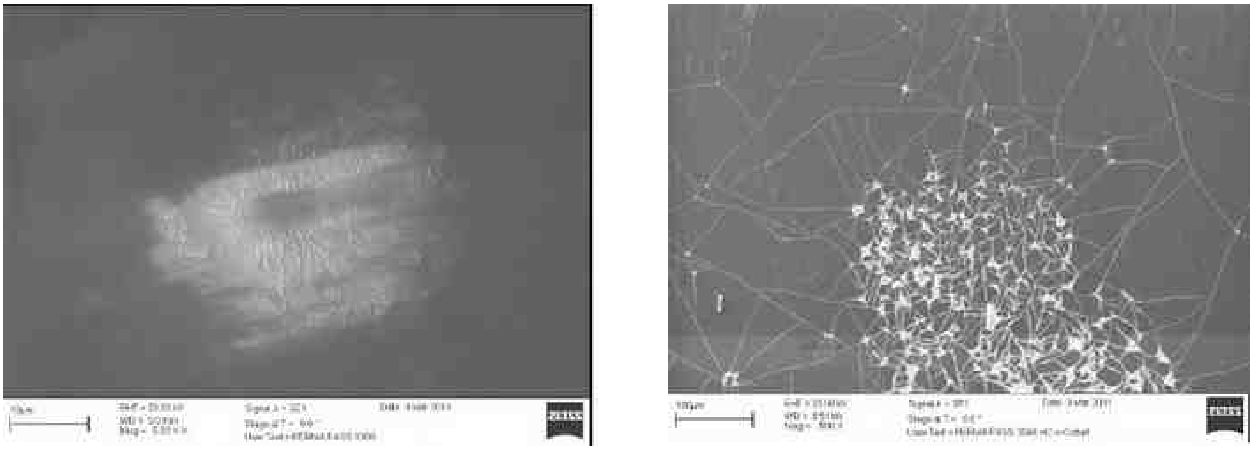

Figure 6 - SEM photos from passivate defect areas: (L) cobalt free passivate; (R) cobalt-containing passivate.

Surprisingly, it was observed that the cobalt-free film showed no cracks in the presence of the introduced defects. The assumption would be that this should actually perform better than the cracked film. An explanation for the reduced performance is that the cobalt-free passivate is not able to generate Cr(VI), which can protect defect areas. The formation of Cr(VI) in cobalt-containing passivates is nothing new. It has been published in 2007 by Rochester, *et al.* and Miura.[10-12] So the better performance of the cobalt-containing passivates in corrosion tests is related to the formation of "helpful" Cr(VI).

Tests according to DIN-ISO 3613[13] prove the presence of Cr(VI) in cobalt-containing passivates (Fig. 7). The color results from the reaction of diphenycarbazide with Cr(VI). The results clearly show that cobalt-containing passivates generate Cr(VI) and the cobalt-free passivates do not.

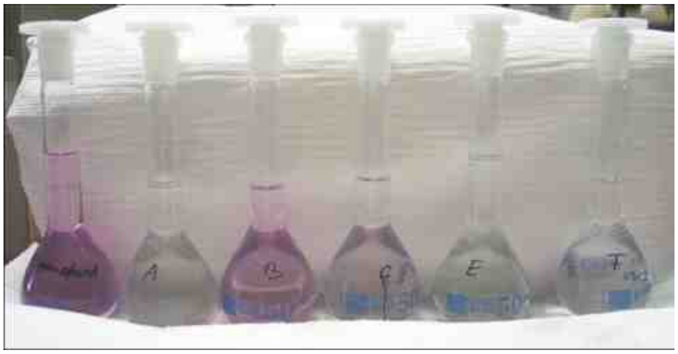

Figure 7 - Test according ISO 3613:[13] (L) = Reference solution; (A) = Cobalt-free passivate; (B) = Cobalt-containing passivate I; (C) = Cobalt-containing passivate II; (E) = Cobalt-free passivate after three months storage; (F) = Cobalt-free passivate after one week storage.

Overcoming the “weakness” of not “healing” defects with Cr(VI)

To overcome the fact that the new cobalt-free passivate does not generate Cr(VI), post-dips can be used. Tests with inorganic Cr(VI)-free and cobalt-free post-dips led to corrosion protection performance similar to that of cobalt-containing passivates.

Summary

The new cobalt-free passivate technology offers similar corrosion protection and similar handling when compared to the traditional cobalt-containing thick film passivates. In addition, the appearance is significantly improved. The new system can replace the “old” passivates. However, in circumstances where there are surface defects, the cobalt-containing passivates perform better, due to the generation of small amounts Cr(VI). The cobalt-free technology does not produce Cr(VI). However, with the application of post-dips, corrosion protection similar to that of cobalt-containing passivates can be achieved.

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