Organic Corrosion Inhibitors for Acidic Media

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Abstract: The control of metal ablation in acidic treatment baths and the prevention of uniform corrosion on metal parts after the use such baths are closely related key technologies that are being challenged by increasingly complex legal requirements. This is reflected by the ban or the de-facto abandonment of various well-tried corrosion inhibiting actives and by the demand for better corrosion protection in simplified manufacturing processes. There is a large potential for improvement through the use of organic corrosion inhibitors. This paper presents experimental results on the effect of acetylene derivatives, a cationic polymer and other active ingedients on corrosion in acidic media. The potential of two of these inhibitors is exemplified with data on their use in a pickling bath and in a post treatment bath. In chromate-free post treatment baths, uniform corrosion on the inside of hollow parts can be effectively prevented through the use of minimal doses of corrosion inhibitors. Immersion tests, weathering, and electrochemical measurements are used to monitor the effect of the inhibitors and their synergy with other additives.

Introduction

Chromate has been banned from the use in electric appliances and cars through legislations that have or will come into effect in Europe. This ban affects the industry worldwide due to international trade and global supply chains. Chromate plays an important role in the finishing of zinc-plated steel. In the form of an acidic rinse and in conjunction with a variety of other actives, chromate has been used as post-treatment that prevents the formation of white rust on zinc. In an effort to replace chromate in this application, a huge variety of alternatives has been suggested. One system that receives particular attention

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throughout the industry is based on chromium(III) salts. Acidic chromium(III)-based formulations are used as so called "Cr(III) thick-layer passivation" in finishing of zinc-plated parts. Some Cr(III) thick-layer passivations do actually match the high corrosion protection level of former chromate-based treatments. One drawback in the use of Cr(III) passivations is observed in plating of hollow parts. As the hollow part acts like a Faraday's cage during electrodeposition, its inside is not plated with zinc. When the hollow part later is treated with an acidic Cr(III) passivation, this will result in two unwanted side effects: *(i)* The acidic solution attacks the non-plated steel surfaces and liberates iron salts that affect the passivation treatment. *(ii)* The acidic attack on the non-plated steel yields uniform corrosion on the inner, non-plated surface of the hollow part.

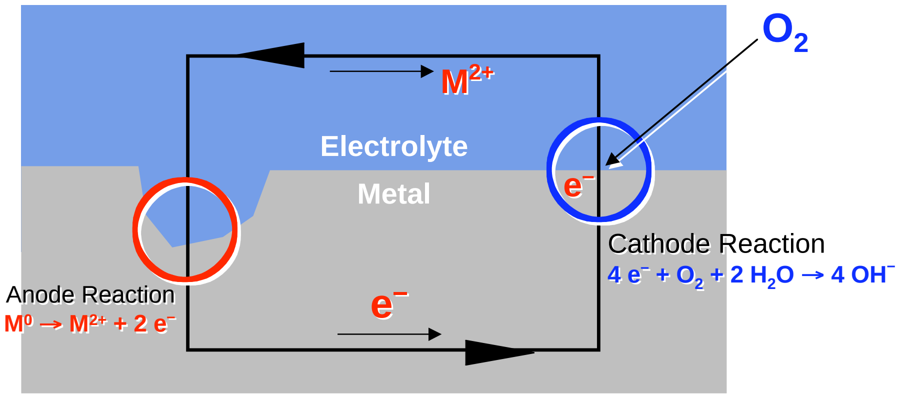
Organic corrosion inhibitors play an important role in metal surface treatment with acidic media. For instance, corrosion inhibitors like propargyl alcohol and butynediol are used with hydrochloric acid or sulfuric acid for pickling of steel. The role of the inhibitor here is to minimize metal ablation while not affecting the scale and rust removing process through the acid. In galvanic baths, plating additives are employed that have a potential to function as corrosion inhibitors as well. While extensive information is available on the use of organic corrosion inhibitors for metal surface treatment, only few reports are available on the use of organic corrosion inhibitors as part of passivation treatments. This may in part have to do with the fact that the arbitrary addition of a corrosion inhibitor to a passivation bath is expected to interfere with the passivating reaction, i. e. the controlled dissolving of a metal and the subsequent formation of an insoluble salt of the metal on the surface

It is the target of this report to show the potential of corrosion inhibitors as additives in Cr(III)-based passivations in order to prevent tarnishing and corrosion inside electroplated hollow parts.

Function of Corrosion Inhibitors

Corrosion is an electrochemical process that can be described as an electric circuit comprising an anode, where a metal dissolves as cation, and a cathode where — depending on pH — oxygen from air is reduced to hydroxide or protons from the solution are reduced to hydrogen (Fig. 1). The chemical reaction occurring at the anode and the cathode are subject to the influence of corrosion inhibitors. Inhibitors affecting the anode reaction are called anodic inhibitors. Inhibitors affecting the cathode reaction are called cathodic inhibitors. Anodic inhibitors are for instance compounds that form insoluble salts with the corroding metal. Through precipitation, they block the anodic site from further attack through corrosive media. Cathodic inhibitors for instance act through precipitation on the cathodic site due to a pH increase caused by the corrosion reaction. Anodic and cathodic inhibitors can be identified through electrochemical measurements.

***Fig. 1:** Schematic illustration of a corrosion process.*



$$M^0 \rightarrow M^{2+} + 2\ e^-$$

$$4\ e^- + O_2 + 2\ H_2O \rightarrow 4\ OH^-$$

$$2\ M + O_2 + 2\ H_2O \rightarrow 2\ M(OH)_2$$

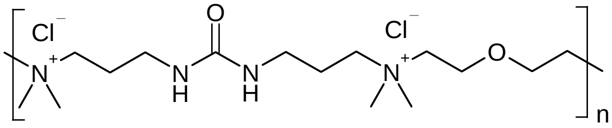
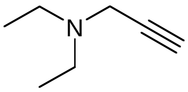
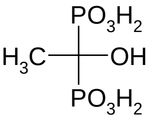
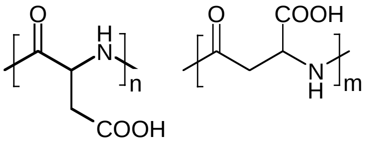
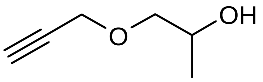
Selection of Corrosion Inhibitors for Acidic Media

In order to identify a suitable additive for Cr(III) passivations, various corrosion inhibitors are screened. The selection criteria comprise

- anti-corrosiveness
- tolerance against saline media and high concentrations of multivalent cations
- favorable toxicological properties

A selection of corrosion inhibitors that are considered is listed in Tab. 1.

***Tab. 1:** Selection of organic corrosion inhibitors*[2].

Entry	Chemical Name	Chemical Structure
CP	cationic polyurea	
DEP	N,N-diethylpropargyl amine	
HEDP	1-hydroxyethylidene-1,1-phosphonic acid	 $H_3C-C(PO_3H_2)_2-OH$
P(ASPA)	polyaspartic acid	
PA	propargyl alcohol	$HC\equiv C-CH_2-OH$
PP	ethinylcarbinol propoxylate	

The anticorrosive effect of various organic corrosion inhibitors is tested in an immersion test. Steel coupons (S235JR, 10 cm x 2 cm) are immersed into hydrochloric acid (pH 2) at 80°C for 6 hours. The anti-corrosive effect is determined as corrosion inhibition efficiency

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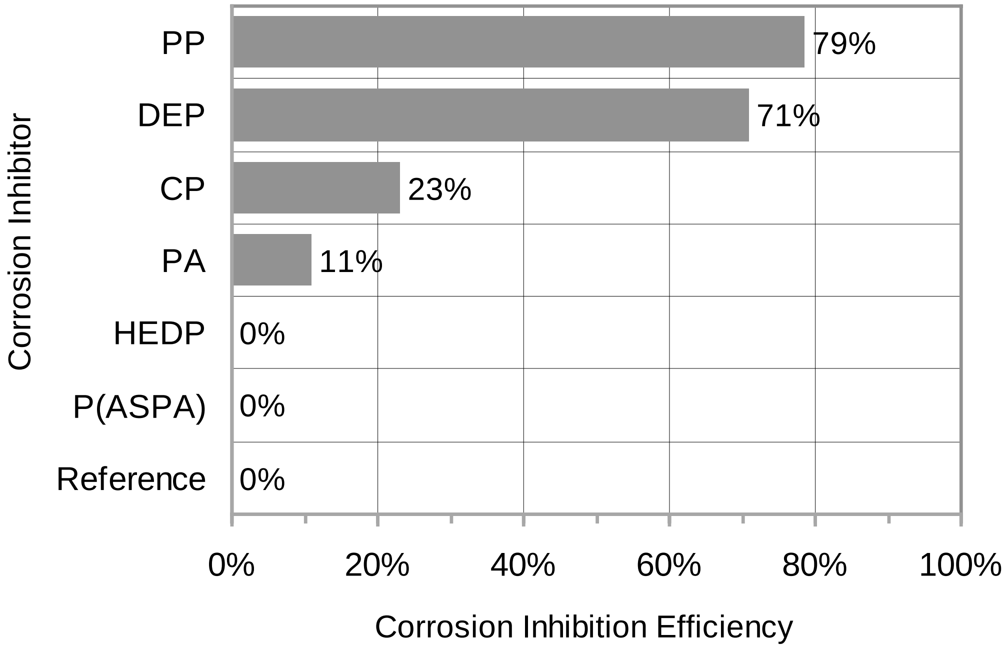
[2] HEDP, P(ASPA), and PA are available from lab chemicals suppliers. CP is available as Lugalvan® P from BASF Corporation, Florham Park, NJ. DEP is available as Golpanol® DEP from BASF Corporation, Florham Park, NJ. PP is available as Korantin® PP from BASF Corporation, Florham Park, NJ. Golpanol, Korantin, and Lugalvan are registrated trademarks of BASF Corporation, Florham Park, NJ, and of BASF Aktiengesellschaft, Ludwigshafen, Germany.

$$CI = \Delta m_i - \Delta m_0 / \Delta m_0$$

where Δm_i is the mass loss of the coupon after immersion in the corrosive medium with corrosion inhibitor and Δm_0 is the mass loss of a reference after immersion in the corrosive medium without corrosion inhibitor. The results of the corrosion test are summarized in Fig. 2. Acetylene derivatives like PP and DEP clearly reveal a much stronger anticorrosive effect as compared to propargyl alcohol, PA, a standard pickling inhibitor for treatment of steel in acids. The cationic polymer CP reveals an anticorrosive effect stronger than PA but not as strong as PP and DEP. Anionic species like the phosphonate HEDP and the polyamino acid P(ASPA) do not exhibit an anticorrosive effect.

Fig. 2: *Corrosion inhibiting efficiency of organic corrosion inhibitors (1% w/w actives) in hydrochloric acid (pH 2, 80°C), on S235JR steel after 6 hours immersion.*



Another criterion in this study is the mechanism of corrosion inhibition. It is the goal of this study to compare the effects of an anodic and a cathodic corrosion inhibitor on a passivating bath. The corrosion inhibiting effect as measured in a cyclic polarization experiment is depicted in Figs. 3-5. Comparison of the data indicates that the ethinylcarbinol propoxylate PP functions as an anodic corrosion inhibitor whereas the cationic polyurea CP is a cathodic corrosion inhibitor.

Fig. 3: *Cyclic polarization*[3] *of X5CrNi18-10 steel*[4] *in water containing 1.6 % w/w HCl and 2% NaCl.*

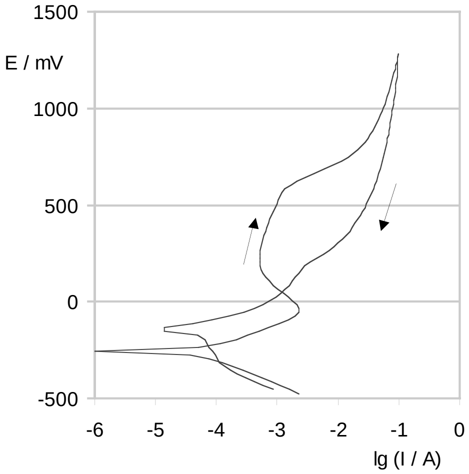
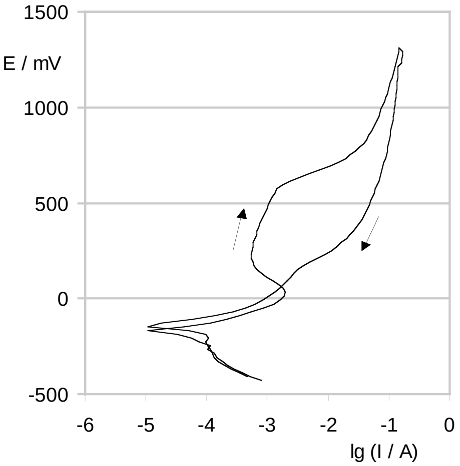


Fig. 4: *Cyclic polarization of X5CrNi18-10 steel in water containing 1.6 % w/w HCl and 2% NaCl with a corrosion inhibitor, ethinylcarbinol propoxylate, PP, 0.05% w/w actives.*



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[3] All polarization experiments have been carried out with commercially available potentiometer at a scan rate of 10 mV/s. Ag/AgCl (3 M KCl) is used as a reference electrode. All voltage data refers to this standard. The test electrode area is 1 cm^2.

[4] X5CrNi18-10 is the same as 304 (H) steel.

Fig. 5: *Cyclic polarization of X5CrNi18-10 steel in water containing 1.6 % w/w HCl and 2% NaCl with a corrosion inhibitor, cationic polyurea, CP, 0.05% w/w actives.*

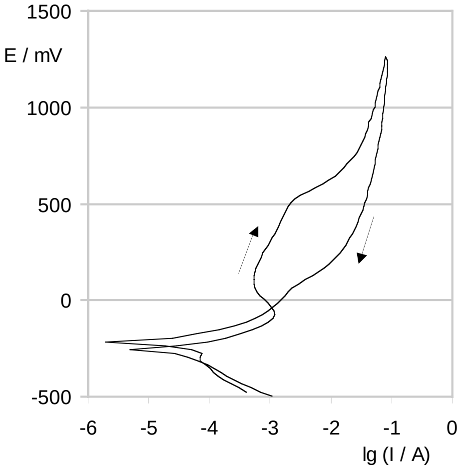
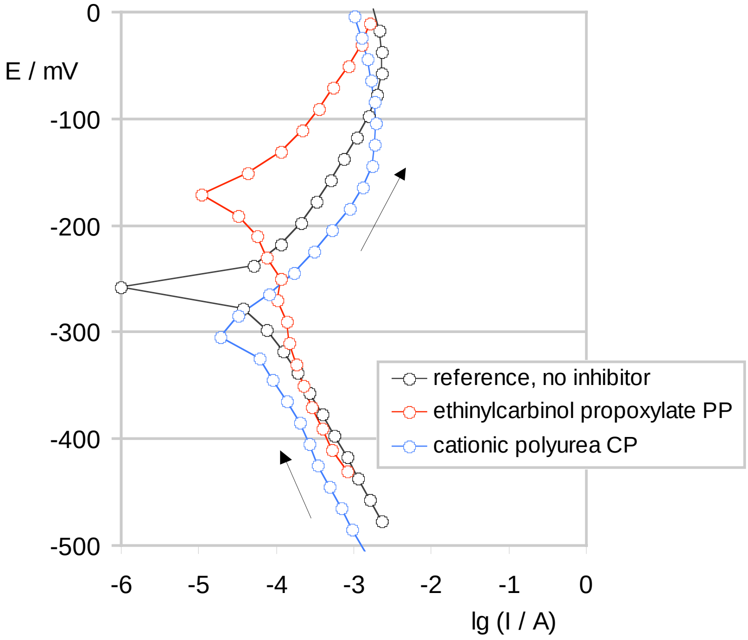


Fig. 6: *Overlay of Figs. 3-5. Accelerating voltage branch close to the open-circuit potential.*



The results from corrosion testing and other properties affecting the feasibility for use as a bath additive are summarized in Tab. 2. Based on this summary, ethinylcarbinol propoxylate PP and the cationic polyurea CP are selected for further testing as additives in Cr(III)-based passivations.

Tab. 2: *Comparison of organic corrosion inhibitors with respect to their feasibility as corrosion inhibitors and as bath additives.*

Entry	Chemical Name	Corrosion Protection[5]	Tolerance Against Multivalent Cations	Toxicological Properties
CP	cationic polyurea	+ cathodic inhibitor	++	+
DEP	N,N-diethylpropargyl amine	++	++	+
HEDP	1-hydroxyethylidene-1,1-phosphonic acid	0	++	+
P(ASPA)	polyaspartic acid	0	+	+
PA	propargyl alcohol	+	++	– toxic
PP	ethinylcarbinol propoxylate	++ anodic inhibitor	++	++

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[5] according to conditions described in Figs. 2-6

Cr(III) Passivation with Organic Corrosion Inhibitors

In order to mimic the influence of a Cr(III) passivation treatment on the inside of galvanized hollow parts, non-plated steel coupons (steel DC01) are immersed into a commercially available Cr(III) passivation bath[6] with and without addition of an inhibitor to the bath. Steel DC01 is dipped for 60 sec into the bath (60°C, pH 1.8), removed, dried under ambient conditions, and stored for six days. The surface develops a distinct discoloration during drying when no inhibitor is used. When corrosion inhibitors are used, no discoloration and no iridescence are seen (Figs. 7-9). At a concentration of 0.01% w/w of the cationic polyurea CP, tarnishing is completely prevented. At a concentration of 0.1% w/w tarnishing is prevented with both, the cationic polyurea CP and ethinylcarbinol propoxylate PP.

The tendency of rust formation is evaluated through climatic cycling of steel coupons from the aforementioned test. For this purpose, the test coupons are exposed to one climatic cycle comprising a period of 8 h / 35°C / 100% relative humidity and 16 h / 20°C / 50% humidity. Without corrosion inhibitor, a uniform pattern of corrosion pits is observed. Both, the cationic polyurea CP and ethinylcarbinol propoxylate PP, considerably decrease the number of pits when used at a concentration level of 0.01% and 0.1% w/w respectively in the passivation bath. At a concentration of 0.1% w/w of the cationic polyurea, pit formation is almost completely prevented (Figs.10-13). The cationic polyurea CP is further evaluated regarding its effect on the C(III) passivation treatment on zinc-plated steel.

In order to evaluate whether the addition of the cationic polyurea CP interferes with the function of the passivation bath, salt spray testing of galvanized steel sheets is carried out. After 48 hrs of salt spray testing according to ASTM B 117-97, no white rust formation is seen on test coupons that have been passivated with a Cr(III)-based bath with and without the cationic polyurea CP. After 72 h, initial white rust develops, regardless of whether or not the corrosion inhibitor has been used in the Cr(III) passivation bath (Fig. 14).

Conclusions

The formation of red rust inside of Cr(III)-passivated, galvanized steel hollow parts is a severe problem. According to this lab study, the use of corrosion inhibitors provides a tool to overcome this difficulty. Two corrosion inhibitors, a cationic polyurea (CP) and ethinylcarbinol propoxylate (PP) are used successfully to minimize tarnishing and rust formation on blank steel surfaces that have been exposed to a Cr(III) passivation treatment. With the cationic polyurea CP, a considerable anticorrosive effect is found at a

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[6] Acidic, chromate-free passivation bath based on chromium(III) nitrate, cobalt(III) nitrate, and sodium oxalate.

concentration as low as 0.01% w/w in the passivation bath. Red rust formation on non-plated steel can be almost completely prevented with this inhibitor at a concentration level of 0.1% w/w. The addition of this corrosion inhibitor does not interfere with the function of the Cr(III) passivation on zinc-plated steel.

Fig. 7: *Steel coupon (DC01 steel, 10 cm x 10 cm) after immersion into a Cr(III) passivation bath*[6]*. Left: Without addition of a corrosion inhibitor. Right: With 0.01% w/w cationic polyurea CP as bath additive.*

Fig. 8: *Steel coupon (DC01 steel, 10 cm x 10 cm) after immersion into a Cr(III) passivation bath*[6]*. Left: Without addition of a corrosion inhibitor. Right: With 0.1% w/w cationic polyurea CP as bath additive.*

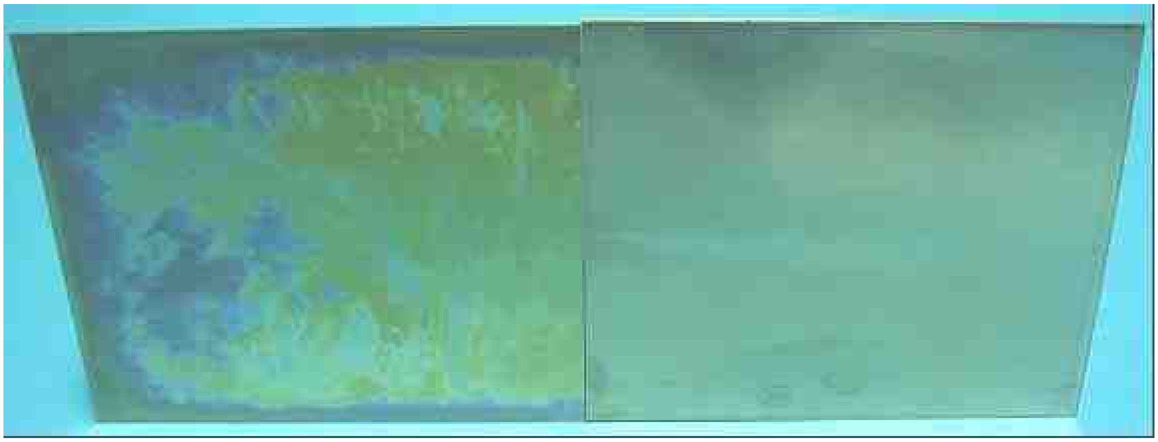

Fig. 9: *Steel coupon (DC01 steel, 10 cm x 10 cm) after immersion into a Cr(III) passivation bath*[6]*. Left: Without addition of a corrosion inhibitor. Right: With 0.1% w/w ethinylcarbinol propoxylate PP as bath additive.*

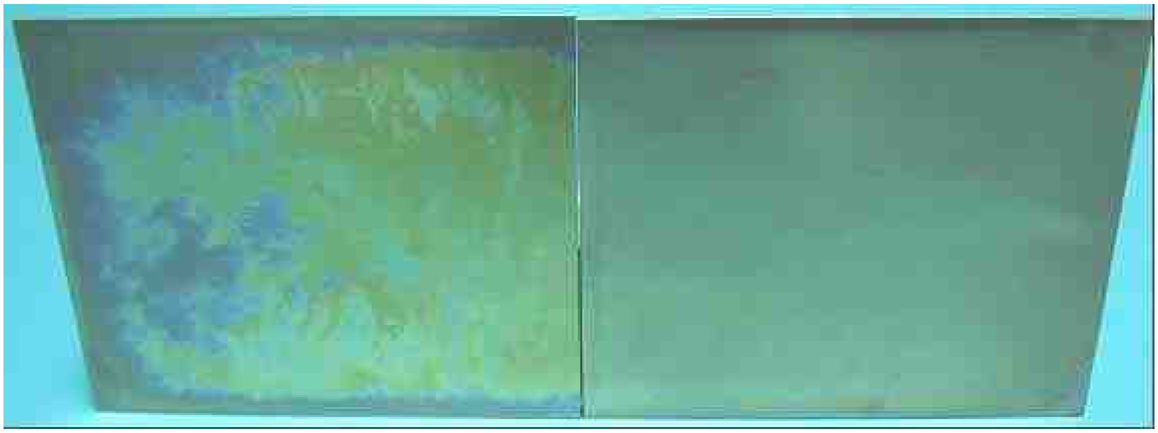

Fig. 10: *Steel coupon (DC01 steel, 10 cm x 10 cm) after immersion into a Cr(III) passivation bath*[6] *and subsequent exposure to a humid-dry cycle. Left: Without addition of a corrosion inhibitor. Right: With 0.01% w/w cationic polyurea CP as bath additive.*

Fig. 11: *Steel coupon (DC01 steel, 10 cm x 10 cm) after immersion into a Cr(III) passivation bath*[6] *and subsequent exposure to a humid-dry cycle. Left: Without addition of a corrosion inhibitor. Right: With 0.1% w/w cationic polyurea CP as bath additive.*

Fig. 12: *Steel coupon (DC01 steel, 10 cm x 10 cm) after immersion into a Cr(III) passivation bath*[6] *and subsequent exposure to a humid-dry cycle. Left: Without addition of a corrosion inhibitor. Right: With 0.01% w/w ethinylcarbinol propoxylate PP as bath additive.*

Fig. 13: *Steel coupon (DC01 steel, 10 cm x 10 cm) after immersion into a Cr(III) passivation bath*[6] *and subsequent exposure to a humid-dry cycle. Left: Without addition of a corrosion inhibitor. Right: With 0.1% w/w ethinylcarbinol propoxylate PP as bath additive.*

Fig. 14: *Steel coupon (electrogalvanized steel) after immersion into a Cr(III) passivation bath*[6] *and subsequent exposure in a 72 h salt-spray test. Right: Without addition of a corrosion inhibitor. Left: With 0.1% w/w cationic polyurea CP as bath additive.*