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# Chromate-free smart release corrosion inhibitive pigments containing cations

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ABSTRACT

A smart release chrome-free inhibiting system is utilised in an organic coating system to inhibit cathodic disbondment of hot dip galvanised steel. The non-toxic smart release cation system is relatively cheap, easy to process and highly effective. An in-situ scanning Kelvin probe is used to assess the protection offered by the cation containing pigments in a poly-vinyl-butyral model coating. The inhibition of cathodic delamination under the SKP testing conditions exceeds that of hexavalent chromate by the inhibitor system containing magnesium(II) ions.

## 1. Introduction

The inclusion of smart-release vehicles within coatings has relieved the constraint of inhibiting species forming part of sparingly soluble salts, to reservoirs of corrosion inhibiting ions that previously would not be considered as part of a primer system. The current chrome free inhibitor Shieldex® is an ion exchanged amorphous silica, that has a reservoir of $Ca^{2+}$ ions, that are released in response to cations in the environment. It is stated by the manufacturer that in alkaline environments, the amorphous silica will more readily dissolve [1], which is thought to form a protective layer via a hydrated silica gel and metal oxide in the case of iron or possibly zinc silicate anodically inhibiting dissolution of zinc [2]. The inhibitory effects of Shieldex® have been the focus of many investigations [3–6] to assess if it is a contender in replacing hexavalent chromate at protecting iron and zinc substrates, and the mechanisms of action are considered to be; to trap or delay the aggressive ions getting to the metal surface by exchanging them for $Ca^{2+}$ ions, improve cross-linking of the binder, silica and calcium become mobile within the coating and form a protective film on the metal surface [7]. Previous investigations assessing cations as inhibitors have focussed on in-solution cation corrosion inhibitors for zinc [8,9] and the doping of silane pretreatments with rare earth cations to improve the barrier and corrosion properties [10]. Williams et al. investigated the use of cations within the coating to inhibit cathodic disbondment of hot dip galvanised steel (HDG), firstly in naturally occurring Wyoming bentonite clays [11] and later cross-linked sulphonated polystyrene (CSP) [12]. The poor compatibility of bentonite clays and organic coating systems meant that the CSP Dowex® or similar could be viable ‘smart’ replacements for hexavalent chromate systems.

Cathodic disbondment is the main failure mechanism of organically coated HDG investigated here, and the zinc corrosion cell is simplified into the anodic reaction (Eq. (1)) and cathodic reaction (Eq. (2)).

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{1}$$

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

The anodic metal dissolution reaction takes place within the defect and the cathodic oxygen reduction reaction takes place under the film at the disbondment front. The elevated pH within the disbonded underfilm environment results in an anodic reaction leading to zincate formation [13,14], as shown in the pourbaix diagram, where pH above ca. 10.5 leads to bizincate and at higher pH, zincate.

The formation of zincate initiates with the dissolution of the zinc(hydr)oxide surface layer, producing soluble bizincate

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($HZnO_2^-$) and zincate ($ZnO_2^{2-}$) by the following equilibrium reactions,

$$Zn(OH)_{2(s)} \rightleftharpoons HZnO_2{}^-{}_{(aq)} + H^+{}_{(aq)} \quad (3)$$

$$Zn(OH)_{2(s)} \rightleftharpoons ZnO_2{}^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \quad (4)$$

for which the solubility product ($K_{sp}$) values for the most soluble (amorphous) form of $Zn(OH)_2$ at 25 °C are $4.27 \times 10^{-16}$ $M^2$ and $1.07 \times 10^{-30}$ $M^3$ [15]·

The mechanism by which certain divalent metal cation ($M^{2+}$) are principally thought to inhibit cathodic disbondment is through the formation of insoluble metal hydroxides by hydrolysis or partial hydrolysis of $M^{2+}$ by Eqs. (5) and (6):

$$[M(H_2O)_6]^{2+} \rightleftharpoons [M(H_2O)_6OH]^+ + H^+ \quad (5)$$

$$M^{2+} + 2H_2O \rightleftharpoons MOH_2 + 2H^+ \quad (6)$$

This results in the reduction of the under film conductivity and decreases the ion mobility. Others have also argued that in the case of $Ca^{2+}$ cations, the zincate anions formed in the high alkalinity of the cathodic disbondment corrosion cell can also react with the $M^{2+}$ ions to form insoluble $M(OH)_2{\cdot}2Zn(OH)_2{\cdot}2H_2O$ or $MZn_2(OH)_6{\cdot}2H_2O$ and thus also reduce underfilm conductivity [11].

To continue previous investigations [11,16], a different matrix system was utilised to store cations, investigating the effectiveness of the cations at inhibiting the corrosion driven cathodic delamination of coated HDG. The matrix used was a crosslinked divinyl benzene matrix with a sulphonated functional group, with a commercial name of Amberlite®. The form used was the IR120 which has a $H^+$ counterion making it a strongly acidic ion exchanger. The sulphonate maintains a negative charge and will hold the inhibiting cation in place until the matrix is in contact with a solution containing cations that it will exchange the inhibiting cation for. The use of such ion exchange matrices are common place in effluent discharge for the removal of metal cations such as $Ni^{2+}$, $Zn^{2+}$, $Ca^{2+}$ and $Mg^{2+}$ [17,18]. The previous work looking at Dowex® as the exchange matrix, utilised a number of cations to be used as inhibitors and the current research assesses the effect of changing the counterion from $Na^+$ to $H^+$ making it a stronger acidic exchanger. The aims of the investigations are:

i) To answer does having $H^+$ as the counterion affect the exchange efficiency and in turn increase the inhibition when the same cation is used.
ii) To determine the effect of a wider range of potential inhibitors, to include group II cations to identify the relative importance of the formed hydroxide solubility product at inhibiting cathodic delamination.

## 2. Experimental details

### 2.1. Materials

Hot dip galvanised (HDG) steel samples consisting of 0.7 mm gauge mild steel coated on both sides with a 20 μm zinc layer containing 0.15 wt.% aluminium were supplied by Tata Steel UK. Amberlite® IR120 ($H^+$ form), Amberjet® 4200 ($Cl^-$ form), sodium chromate 98%, calcium chloride dihydrate ACS reagent, ≥99%, barium chloride dehydrate ACS reagent, ≥99%, magnesium chloride hexahydrate BioXtra, ≥99.0% and strontium chloride hexahydrate ACS reagent >99%, cerium(III) chloride hexahydrate ≥98.0%, cobalt(II) chloride hexahydrate ACS reagent 98%, polyvinylbutyral-*co*-vinyl alcohol-*co*-vinylacetate (PVB), molecular weight 70,000–100,000, were obtained from the Sigma Aldrich Chemical Company.

### 2.2. Methods

A 0.5 M stock solution of each of the metal chloride solutions and sodium chromate solution was made using deionised water, the solutions were added to the resin beads in the ratio of 100 ml per 10 g of Amberlite® IR120 (cations) or Amberjet® 4200 (chromate) resin beads. Each solution and bead mixture was agitated via stirring for 2 h, after which the solution was decanted and replaced with fresh stock solution in the same 100 ml per original 10 g weight ratio. The solutions were stirred for a further 2 h and again the solution was replaced for fresh stock of 0.5 M target metal chloride solution. The beads were left overnight under stirring to ensure maximum exchange had taken place. The beads were filtered using a Buchner filtration system and washed with 500 ml of deionised water, to ensure any chloride solution was removed. The beads were dried for 12 h at 40 °C and then milled using a Retsch planetary ball mill at 350 RPM for 1 h and sieved through a 20 μm mesh. Fig. 1 shows the as delivered Amberlite® beads (a), typically 680–820 μm in diameter and after processing with the cation exchanged into the matrix (b) with a diameter of <20 μm.

The mass of the pigment required for each pigment volume fraction (PVF) was ascertained using:

$$M_{pig} = \frac{\phi \times M_{pol} \times \rho_{pig}}{(1-\phi) \times \rho_{pol}} \quad (7)$$

where $M_{pig}$ is mass of pigment, $M_{pol}$ is mass of polymer, $\rho_{pig}$ is the density of pigment, $\rho_{pol}$ is the density of polymer and $\phi$ is

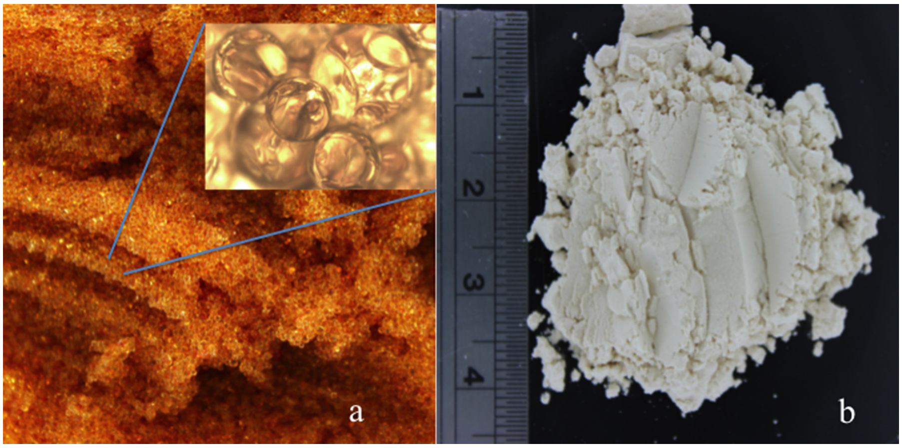

**Fig. 1.** Amberlite® IR120 resin beads in as delivered form (a) and after processing with the addition of inhibiting cation (b).