

## BEHAVIOR OF CONTROL AND INHIBITIVE POLYASPARTIC COATINGS USING ALKYLAMMONIUM AND ZINC PHOSPHATE CORROSION INHIBITORS IN SOIL

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This study is part of an anti-corrosion coating development project at CHEMSYSTEMS. The corrosion performance was assessed through erosion, immersion and soil corrosion experiments. The erosion results have previously been published. This article discusses the impact of soil on control polyaspartic coatings used to protect concrete and the modified polyaspartic coating intended to protect underground steel substrates. The modified polyaspartic coating was boosted with a micaceous iron oxide barrier, a liquid alkylammonium corrosion inhibitor, a powdered zinc phosphate corrosion inhibitor and a novel hardener. The surface finish of the steel samples was of a milled and blasted nature (SA 2.5). The coating was applied directly to the metal without the application of a primer or second layer of coating. The average thickness of the coating was  $220 \pm 10 \mu\text{m}$  as a direct-to-metal protection system. The experiments were conducted in soil at room temperature (RT) and  $35^\circ\text{C}$  over 30 days. The experimental results of the control polyaspartic coating loaded on steel substrates exhibited severe blistering. The polyaspartic coating dispersed with a liquid alkylammonium inhibitor also exhibited blistering, whereas the modified polyaspartic coating with a zinc phosphate corrosion inhibitor showed an adequate degree of resistance to the impact of soil under the evaluated conditions. The results confirmed that the presence of a zinc phosphate corrosion inhibitor in combination with a micaceous iron oxide barrier improved the resistance of the coating to the evaluated soils in which it was positioned and at the investigated temperatures.

**Keywords:** soil, polyaspartic coating, corrosion inhibitor, iron oxide barrier

### 1. Introduction

Carbon steels with desirable mechanical properties are widely used in infrastructure, including in underground assets such as pillars, foundations, storage tanks and pipelines. In the field, these structures are more likely to degrade and rust due to direct contact with the soil, especially if no protection system is provided to hinder the effect of the corrosive elements. Corrosion due to soil is influenced by the temperature, moisture content, oxygen content, environmental pH, microbial activity and soluble salts. Soil moisture contains a wide range of chemicals which have penetrated through the soil surface. Some examples of these chemicals are salts, e.g. chlorides, nitrates, nitrites, sulfates, etc., and heavy metals, e.g. cadmium, chromium, copper, iron, manganese, nickel, lead, zinc, etc. Along with the influence of microbial activity and environmental factors such as temperature, pH, conductivity and dissolved oxygen concentration, salts and heavy metals make the study of soil moisture an interesting topic as they are related to the corrosion of underground metal structures [1]. Jiao Chen et al. 2015 [2] studied the soil corrosion of steel as a function of anions in the soil, namely total

soluble salts,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ , and soil nutrition, that is, moisture content, organic matter, total nitrogen, alkaline hydrolysable nitrogen, available phosphorus and available potassium.

Many attempts have been made in this regard to reduce the risk of soil corrosion on submerged steel and concrete structures. Organic, inorganic and metal coatings such as Zn, Al and Ni are considered to be very effective means to protect submerged assets from premature corrosion and degradation [3]-[4]. Corrosion inhibitors in powdered and liquid forms have been incorporated into coatings to enhance their antirust and adhesive characteristics when applied to substrates. Zinc phosphate is commonly dispersed into coating formulae during manufacturing and effectively reduced the tendency of a coating to fail and substrates to rust. Nevertheless, although further investigations are still favorable to evaluate the efficiency of corrosion inhibitors in coatings exposed to soil, in this study, an attempt was made to compare the efficiency of two types of corrosion inhibitors in combination with iron oxide coatings for the purpose of developing control and inhibited polyaspartic coatings in soils at room temperature (RT) and  $35^\circ\text{C}$  applied to milled-surface-finished and sandblasted steels (SA 2.5).

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## 2. Materials and experiments

The study was carried out on polyaspartic coatings applied to structural steel plates. The tested plates composed of hot-rolled steel grade S235, which was chosen due to its wide range of applications in infrastructure projects in Belgium and throughout Europe, were manufactured by ASK Romein Malle NV, a steel company based in Malle, Belgium. The control polyaspartic coating was designed to protect concrete structures, whereas the modified polyaspartic coating containing inhibitors and a barrier was planned to prevent steel from corroding. The surface finish of the steel panels, as received from the supplier, was milled and blasted (SA 2.5). Before blasting, the mill scale was removed by immersing the steel plates in 10% H<sub>2</sub>SO<sub>4</sub> for 30 minutes at 60°C before being cleaned and dried by acetone to ensure a suitable steel surface before blasting. Sand blasting was carried out using a blasting cabinet, while blast cleaning was performed using granular aluminum oxide abrasive media. The steel samples were 150 x 80 x 2 mm rectangular plates. An example of the surface morphology of both the milled and blasted steel surface finishes are displayed in *Figs. 1a and 1b*, respectively.

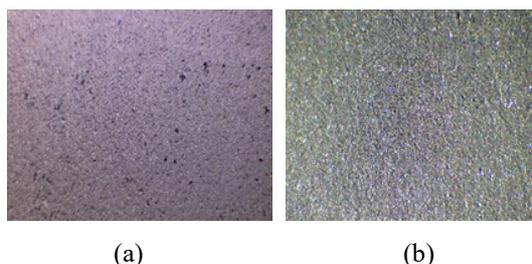


Figure 1. Photographs of a) milled steel finish, b) blasted steel finish

Polyaspartic coatings consist of two components. Component (A), which also contains a corrosion inhibitor and an oxide barrier, is the active material, while component (B) is the hardener. The required amount of component (A) was added to component (B) and mixed for 120 seconds before being applied to the steel. One layer of each coating was applied to each steel sample using an ERICHSEN 358 spiral film applicator and left for one day before being buried in the soil. The edges of the steel samples were well covered with tape to avoid premature failure of the coating or rusting of the steel plates. The edges of the steel plates were carefully smoothed and curved. During the coating, extra layers were applied to the edges, moreover, a strong tape was placed over them to prevent them from rusting and the coating from failing. An example of a coated steel panel is displayed in *Fig. 2*. The soil used in this study was loamy sandy soil according to the Belgian soil analysis report [5] collected from arable, residential and light industrial flattened land located in Malle in the Vlaanderen region of Belgium. The average climate of the soil in the region of Vlaanderen is temperate maritime with an average 800 mm of precipitation falling annually.

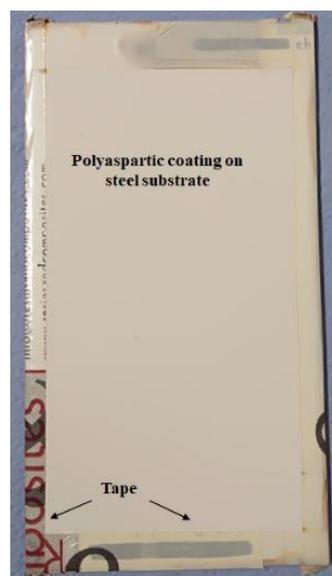


Figure 2: Materials used in the soil experiment: an example of a coated steel panel

In many locations, the concentration of heavy metals in the soil and groundwater still exceeds environmental quality standards due to the use of ash material for road stabilization, which has also resulted in the spread of heavy metals. The actual carbon content of arable land parcels in Flanders is considered to be fairly good. Salinization is a minor concern in the region of the tested soil because it is regarded as being situated far from the coastline [5].

The soil was collected at a depth of 0.5 m and filtered using sieves of two different mesh sizes to remove dirt and purify the soil (*Fig. 3*).

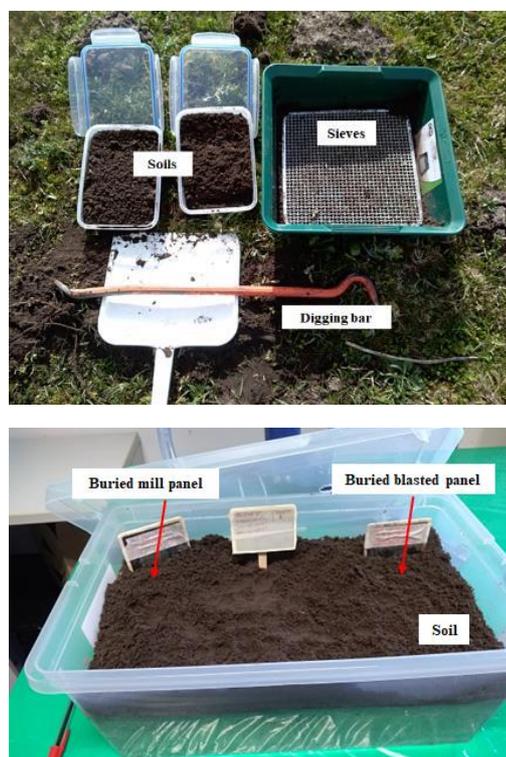


Figure 3: Soil experiment materials: soil collection and coated steel samples buried in soil

The pH of the soil was controlled before each experiment and measured to be between 6.5 and 7.0. The tested samples were placed in soil in a plastic container (Fig. 3) for 30 days at both room temperature and 35°C using an oven. The resistance of the coating to soil attack was evaluated by identifying any forms of coating damage and defects as well as signs of rust on the steel using visual and macroscopic inspection techniques.

### 3. Results and Discussion

Optical observations of the control and inhibited polyaspartic coatings loaded onto milled and blasted steel panels after having been buried in soil for 30 days at RT and 35°C are displayed in Figs. 4-15. The coatings exhibited varying degrees of blistering and, in some cases, some rusting was also present following the test. The experimental results are presented and discussed according to the type of coating applied and the experimental conditions.

#### 3.1. Control polyaspartic coating in soil at RT and 35°C

The macroscopic observations after soil experiments had been conducted on the control polyaspartic coating applied to the milled and blasted surface finished steel panels are depicted in Figs. 4-7. A cluster of blisters on the control polyaspartic coating applied to the milled surface finished steel after a soil experiment had been conducted at RT can be seen in Fig. 4. Furthermore, cracking of the blisters is also clearly visible as indicated by the arrows, where rust can be observed under the peeled off blisters. Additional clustered and isolated open blisters on the control polyaspartic coating tested in soil at 35°C are presented in Fig. 5.

Blisters in isolated spherical shapes of the control polyaspartic coating applied to the blasted, surface finished steel panels are documented in Figs. 6-7. However, in Fig. 6, the surface morphology contains a collection of smaller blisters on the control polyaspartic coating applied to the blasted, surface finished steel after the soil experiments had been conducted at RT. On the other hand, in Fig. 7, bigger blisters on the control

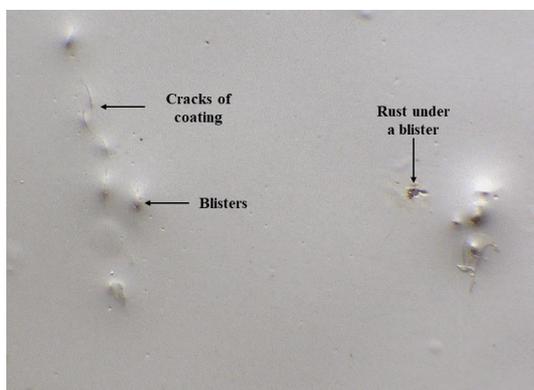


Figure 4. Control polyaspartic coating, milled steel panel, RT

polyaspartic coating are visible following the soil experiments at 35°C.

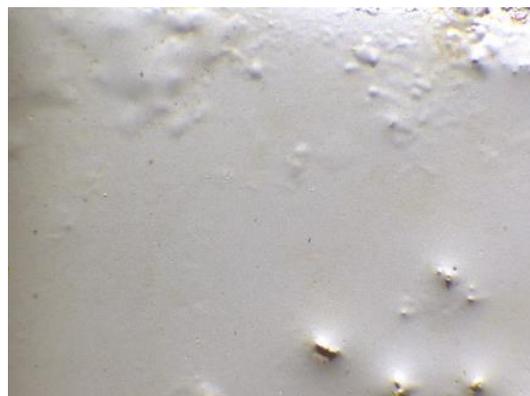


Figure 5. Control polyaspartic coating, milled steel panel, 35°C

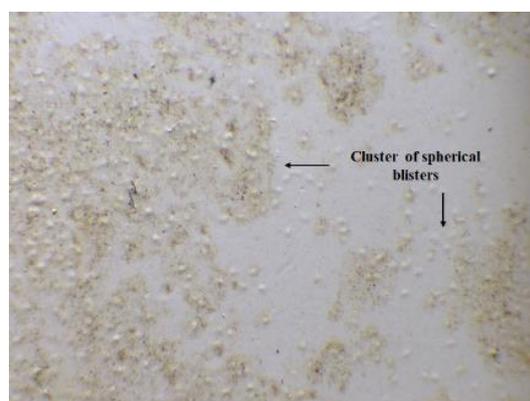


Figure 6. Control polyaspartic coating, blasted steel panel, RT

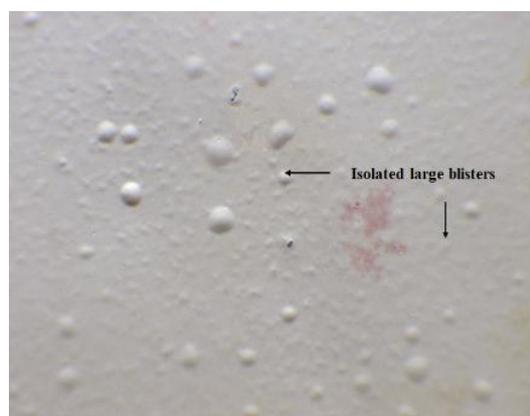


Figure 7. Control polyaspartic coating, blasted steel panel, 35°C

### 3.2. Polyaspartic coating loaded with an alkylammonium corrosion inhibitor tested in soil at RT and 35°C

Corrosion inhibitors are used to reduce the risk of corrosion on metal substrates in aqueous media by forming a barrier film or controlling the corrosion reactions of the corrosion cell. Alkylammonium salt inhibitors exhibit excellent biocidal and anticorrosive properties [6]. Corrosion inhibitors have been added to coating systems as one of the direct additives or in capsular form in the smart coating. Although the addition of a corrosion inhibitor to a coating system is primarily intended to improve its degradation resistance, adhesion between the film coating and metal substrate may also be improved to some extent. Nevertheless, some corrosion inhibitors have a tendency to degrade in microbial cultures such as soils.

In this regard, the performance of the alkylammonium inhibitor in the examined polyaspartic coating submerged in soil is presented in this section. Surface morphological observations of the polyaspartic coating incorporated with the alkylammonium inhibitor and micaceous iron oxide barrier following soil corrosion experiments at RT and 35°C are displayed in *Figs.8-11*. In *Fig.8*, it can be seen that the liquid alkylammonium inhibitor reduced but did not prevent the formation of blisters on the polyaspartic coating applied to the milled surface finished steel panels tested in soil at RT. Perforations through the coatings of the alkylammonium corrosion inhibitor and iron oxide barrier were visible after having been immersed in soil for 30 days at RT.

For clear verification, the images of the perforations were inverted horizontally and vertically as documented in *Figs.8a and 8b*, respectively. Since these perforations were not observed when the coating was applied and before it was immersed in the soil, they may have resulted from the corrosion reactions occurring underneath the coating or the coating substances reacting with the soil causing leaching of coating contents such as the corrosion inhibitors. Groups of blisters and the iron oxide barriers on black spots distributed over the surface of the coating layer can be seen in *Fig.8c*.

As for the samples tested in soil at 35°C presented in *Fig.9*, damage to the coating was in the form of wider bulging blisters, moreover, iron oxide barriers were visible. The effect of the surface finish of the steel panels on the organic inhibitor polyaspartic coating was not noticeable.

However, the degree of blistering still visible on the coating applied to the blasted panels as well as tested in soil at RT and 35°C is illustrated in *Figs.10 and 11*, respectively. The experiments in this study simulated to a certain extent the performance of both steel structures immersed in soil and coatings as one of the most commonly used protection systems for underground assets. In this regard, the examined soils at RT and 35°C were found to threaten the control polyaspartic coating and polyaspartic coating dispersed with the alkylammonium corrosion inhibitor. This outcome is proven by the penetration and accumulation of the

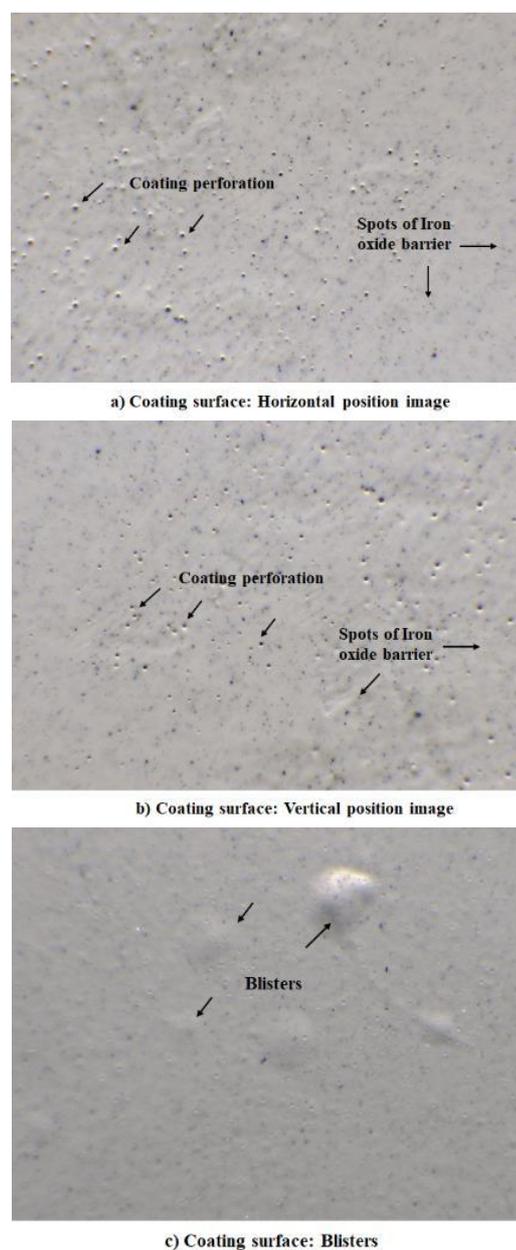


Figure 8. Polyaspartic coating (alkylammonium corrosion inhibitor + iron oxide barrier), milled steel panel, RT

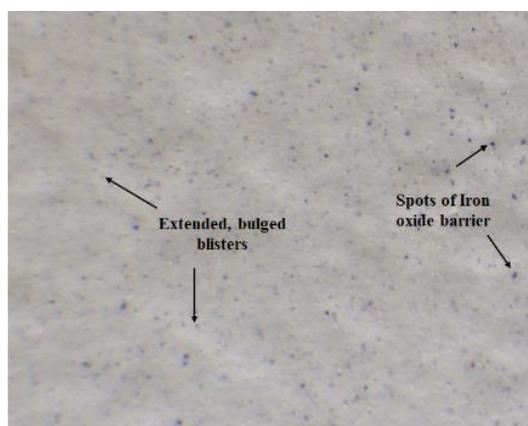


Figure 9. Polyaspartic coating (alkylammonium corrosion inhibitor + iron oxide barrier), milled steel panel, 35°C

aggressive elements in moisture through the coating matrix, whereas the visual and macroscopic interpretations confirmed the existence of a mass of blisters and cracks in the control coating.

The identified blisters in the coating are most likely



Figure 10. Polyaspartic coating (alkylammonium corrosion inhibitor + iron oxide barrier), blasted steel panel, RT

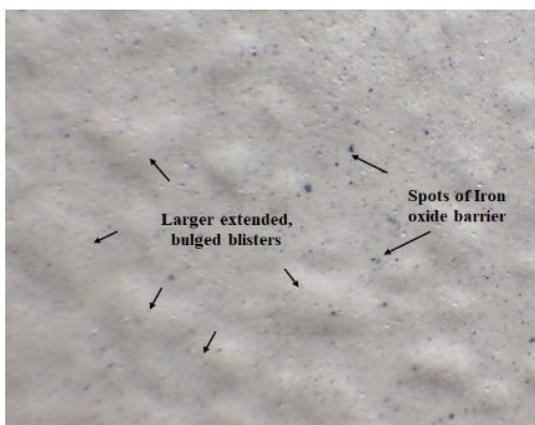


Figure 11. Polyaspartic coating (alkylammonium corrosion inhibitor + iron oxide barrier), blasted steel panel, 35°C

caused by a combination of factors such as saline conditions as well as the presence of sulfate, bacteria and sulfide. The role of such parameters, in addition to chemical, mechanical and biological activities, in the corrosion of buried steel on top of the degradation of other materials are discussed elsewhere [2,7-8]. Furthermore, the microbial culture of the soil has a tendency to cause the biodegradation of the alkylammonium salt that exists in the chains of some corrosion inhibitors in the main structure. This type of biodegradation has been studied by several previous researchers, who summarized that a closely packed nitrogen atom yields biodegradable alkylammonium salts. However, its degree of resistance improves significantly in correlation with the number of long alkyl chains associated with the nitrogen atom [9].

### 3.3. Polyaspartic coating loaded with a zinc phosphate corrosion inhibitor tested in soil at RT and 35°C

Figs.12-15 depict the macroscopic observations of a polyaspartic coating containing a zinc phosphate inhibitor and a micaceous iron oxide barrier applied to milled and blasted steel panels. It was clearly observed that the combination of zinc phosphate and the iron oxide barrier in the polyaspartic coating significantly inhibited the formation of blisters. The optical photographs of the polyaspartic coating tested in soil at RT and 35°C on the milled surface finished and blasted surface finished steel panels are strongly in line with the presence of the zinc phosphate corrosion inhibitor and iron oxide barrier, since neither blisters nor rust were recorded. Only flakes of the iron oxide barrier dispersed in the matrix of the polyaspartic coating are visible. The experimental results show that the dispersion of the zinc phosphate corrosion inhibitor and iron oxide barrier in the polyaspartic coating led to the development of its resistance to soil attack without exhibiting any considerable indications of deterioration. The resistance of this type of coating to the soil is attributed to the effectiveness of the zinc phosphate corrosion inhibitor, which reacted with and bonded to the steel substrate, forming a zinc phosphate protective layer and an iron oxide barrier composed of the phosphating

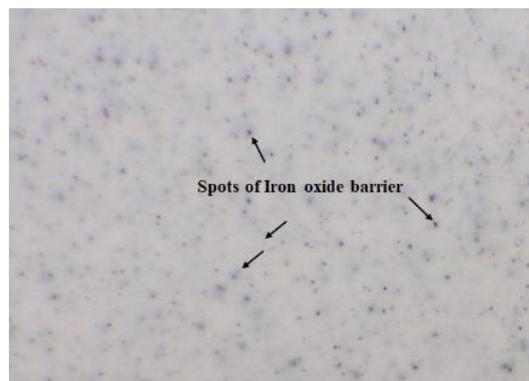


Figure 12. Polyaspartic coating (zinc phosphate corrosion inhibitor + iron oxide barrier), milled steel panel, RT

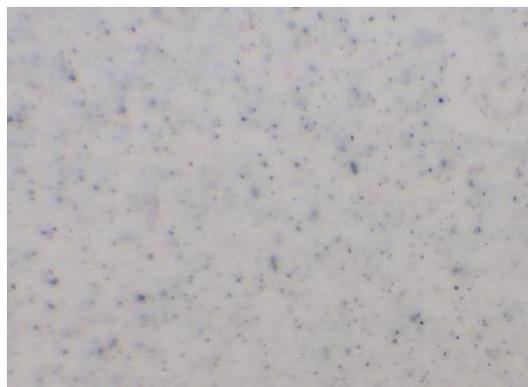


Figure 13. Polyaspartic coating (zinc phosphate corrosion inhibitor + iron oxide barrier), milled steel panel, 35°C

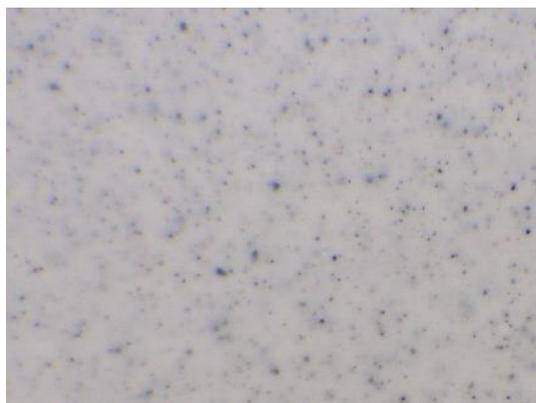


Figure 14. Polyaspartic coating (zinc phosphate corrosion inhibitor + iron oxide barrier), blasted steel panel, RT

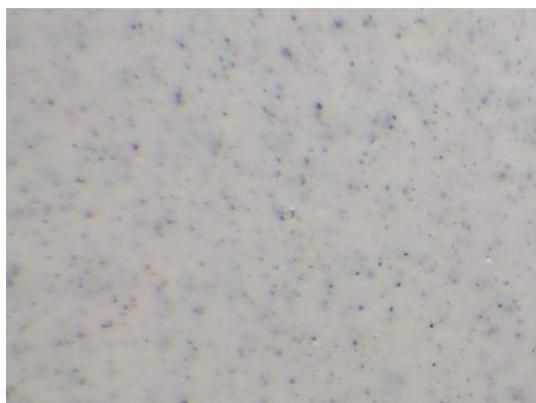


Figure 15. Polyaspartic coating (zinc phosphate corrosion inhibitor + iron oxide barrier), blasted steel panel, 35°C

film containing  $\text{FePO}_4$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$ . The effectiveness of both the zinc phosphate and barrier are in agreement with the findings of several studies that investigated epoxy and waterborne acrylic coatings [10].

### 3.4. Mechanism of blister formation

Blistering phenomena are associated with the absorption of water into the coating. Two of the most common types of coating blisters are: 1) osmotic blisters associated with the diffusion of water through the coating due to the presence of soluble salts on substrates or interlayers; 2) non-osmotic blisters due to swelling and buckling of the coating associated with the absorption of water in the coating [11]. In *Figs.4 and 5*, rust is observed under blisters in the control coating on the milled surface finished steel panels. The blisters on the milled surface finished steel panels can be classified as osmotic blisters because the milled layer might contain impurities resulting in a weak degree of adhesion of the coating to the substrate, thereby leading to the possible formation of blisters given the presence of the penetrated moisture. However, since the same coating on blasted steel yielded isolated blisters, as can be seen in *Figs.6 and 7* after soil experiments were conducted at RT and 35°C, it seems that the steel finish controlled the formation of blisters on the control polyaspartic coating. Horizontal and vertical

flip images of perforations in the alkylammonium coating on milled steel plates following soil tests at RT are depicted in *Figs.8a and 8b*, respectively. These can be explained by either corrosion reactions beneath the coating leading to osmotic blisters and subsequently perforations or reactions between the soil and the contents of the coating yielding perforations in the coating due to leaching of some of its contents such as the corrosion inhibitor. Nevertheless, examination of the coating before being buried in the soil did not exhibit perforations, which were only seen after the soil tests. The same sample in *Fig.8c* shows a group of unperforated blisters.

The hypothesis for the formation of blisters recorded in the experimental results is schematically described in *Fig.16*. How moisture from the soil penetrated through the coating is outlined in *Fig.16a*; with regard to the control coating, which does not contain inhibitive pigments or a coating loaded with the alkylammonium corrosion inhibitor, the moisture can easily pass through the coating into the substrate causing blistering. However, the presence of the zinc phosphate corrosion inhibitor and the iron oxide barrier protected the coating against soil attack (*Fig.16b*). Anyway, high-tech investigative techniques such as SEM could be applied in future studies to better understand the behavior of polyaspartic coatings in soils.

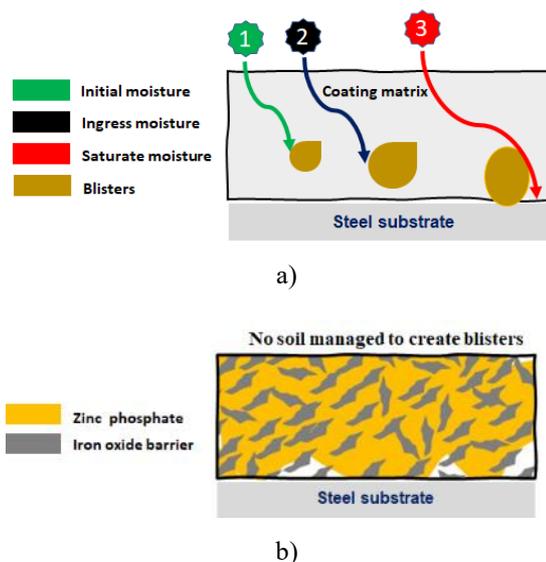


Figure 16. A schematic diagram representing the formation of blisters in the control and inhibitive coatings: a) control coating and b) zinc phosphate + iron oxide barrier inhibitive coating

## 4. Conclusions

Since the content of the coating and temperature are important factors controlling the impact of soil on the performance of coatings and its reliability, the following conclusions have been drawn:

- Increasing the soil temperature from RT to 35°C increased the severity of blistering in the control polyaspartic coating and polyaspartic coating loaded with the alkylammonium corrosion inhibitor after 30-day-long soil experiments due to the high degree of moisture absorption.

- The advantages of applying the zinc phosphate corrosion inhibitor and the micaceous iron oxide barrier are significant in eliminating the soil risk to buried steel.

- This coating efficiently protects milled surface finished steel as well as blasted steel in soil experiments conducted over 30 days at RT and 35°C.

- The newly invented coating formula may well be applied as a protection system for steel assets submerged in soil in industry and the infrastructure sectors.

- The soil experimental results of the polyaspartic coating containing the zinc phosphate corrosion inhibitor supported the final remarks that this type of coating exhibits a good degree of resistance to erosion when immersed, as determined in earlier stages of this project.

Future studies should include experimentally measuring and examining the soil parameters as well as physical testing, which could not be examined at this stage of the project:

1. Soil parameters such as soil type, pH variation, bacterial activity, water content and soil resistivity.
2. Physical and mechanical testing of coatings, e.g. with regard to their compatibility with protective coatings and cathodic protection, cathodic disbondment, flexibility, cracking resistance, electrical and insulation resistance as well as compressive and tensile strength.
3. Thermal resistance and permeability of the coating in the simulation of anticipated working environments.

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