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Understanding the degradation mechanism of painted steel samples as a function of surface characteristics in artificial sea water

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Inadequate surface preparation of mild steel panels prior to painting could be the leading cause of the paint film failure. This work evaluated the surface preparation treatments in order to improve the paint integrity and thereby increasing the corrosion resistance of the steel panel in artificial sea water. The AISI 1020 steel ground and grit blasted samples were prepared followed by applying zinc based epoxy primer and top coat. The degradation mechanism was devised by immersing the samples in 3.5% NaCl solution. The degradation due to blistering within the paint was analyzed by following ASTM D-610 and ASTM D-714. Energy Dispersive Spectroscopy of corrosion product revealed a correlation with the degradation mode of painted sample. It was deduced that degradation of paint depends on surface morphology of substrate.

Key words: Surface preparation, paint, steel, degradation.

INTRODUCTION

Anti corrosiveness is highly important, because corrosion causes structural materials deterioration and destruction includes direct and indirect losses related to natural resources conservation and human safety. The tendency of metals to corrode depends on metal surface characteristics, the metal/protective film interface, the physical, electrical and electrochemical properties of protective films and environmental conditions in which the system is exposed. Steel is widely used as a structural material in different facilities and exposed to aggressive environments. In order to delay or to minimize the deteriorating action of natural or artificial corrosive media, a number of metallic and organic coatings are applied [B.del Amo et al., 2004].

Organic coatings/painting is one of the most common methods for corrosion prevention of steel surfaces as these provide the barrier between a metal surface and environment. Long term protective function of coatings/paint films is dependent on metal coating interfacial characteristics and should maintain adhesion to the metal. Many factors such as poor surface preparation, surface contamination, pin holes in the coating/paint and inadequate paint film thickness may result in loss of adhesion and hence failure occur [Nelson et al., 2012].

Surface preparation affects the performance of coating more than any other variable. Inadequate surface preparation prior to painting is believed to be the leading cause of coating failure. Poor surface preparation particularly results in lower paint adhesion, increased disbondment rate, and increased substrate corrosion rates. In saline solutions the disbondment of organic coating/paints takes place due oxygen reduction reaction at paint/metal interface by the formation of hydroxyl ions which combine with sodium ions and causes increase in pH [Doherty and Sykes, 2008; Castle and Watts, 1985; Leng et al., 1999].

This study has evaluated the usefulness of paint films on alternative surface treatments of metals and thereby identifying corrosion mechanism by increasing anti-corrosive properties. The samples after exposure were

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Table 1. Grit blasting process parameters.

Parameters	Values
Grit condition	Recycled 2 times
Ø of the nozzle	6 mm
Distance between nozzle sample surface	70 - 80 mm
Angle of blasting (π)	70 - 75°
Time of blasting	1 - 2 min

Table 2. Surface parameters of grit blasted surfaces.

Parameter (µm)	R_a	R_z	R_q	R_t	R_p	R_{pc}	R_s	R_{sm}
G02 (G-17)	5.42	41.59	7.14	59.20	18.39	90.12	113	114
G03 (G-20)	3.41	27.96	4.46	37.11	11.82	113.0	82.33	90.33

observed following the standard procedure ASTM D714 for blister formation and ASTM D610 for degree of rusting after every 24 h. This work is a part of larger project and is devoted to study the corrosive properties of different surfaces to understand the degradation mechanism of paint film and its performance in severe corrosive environment.

EXPERIMENTAL WORK

Sample preparation

The three steel panels (100 × 80 × 1.75 mm) were cut from AISI 1020 steel sheet having composition (0.188% C, 0.5% Mn, 0.035% S and Fe balance). One panel G01 was prepared by abrading the surfaces with P600 (Silicon Carbide) grinding paper using portable disk grinder. Other two panels G01 and G02 were grit blasted by two different grit grades G-17 and G-20 respectively to a near white –metal finish (SSPC-SP10). The process parameters were similar for both samples as provided in Table 1. The surface profile of each panel was taken through surface profilometer Mitutoyo SURFTEST SJ.201P/M following the ISO standard. The surface profile parameters measured are given in Table 2.

Surface cleaning

Prior to coating the prepared surfaces were cleaned with acetone to remove any grease or dirt on the surface and then dried in air for 30 min.

Paint application

Lead based epoxy primer (Resin: Hardener = 3:1) was applied at all surfaces under controlled conditions via paint spraying practice and then applied a Lead based epoxy top coat (Resin: Hardener = 3:1) to prime coated surfaces which then placed in a close chamber for 48 h at 38°C and then cured for 200 h in a desiccators at room temperature.

Electrolyte exposure

The cured painted panels were then immersed in artificial aerated sea water (3.5% NaCl solution prepared in de-mineralized water) to analyze the painted surfaces performance under accelerated conditions. The 2/3 portion was immersed in solution while 1/3 portion was out of solution in order to simulate the paint film behavior in the bottom, middle and interfacial. The severity of electrolyte towards paint deterioration was measured in all these zones by visual and microscopic examination. The experimental cell is shown in Figure 1.

RESULTS AND DISCUSSION

Measuring the surface profile

The surface profile parameters for grit blasted samples by two grit grades G-17 and G-20 were correlated with paint film integrity in artificial sea water environment. The average roughness (R_a) produced by grits G-17 and G-20 at the AISI 1020 steel was 5.42 and 3.41 µm respectively. But higher peak count 113 per 2.5 mm sampling length by G-20 as compared to 90 peaks per 2.5 mm sampling length was observed. The values of Arithmetic mean roughness (R_z), Root Mean Square (RMS) Roughness (R_q), Maximum height of the Profile (R_t), Maximum profile height (R_p), Relative roughness of the surface (R_s) and Mean Spacing of Profile Irregularities (R_{sm}) can be compared for both grit grades at the same sample
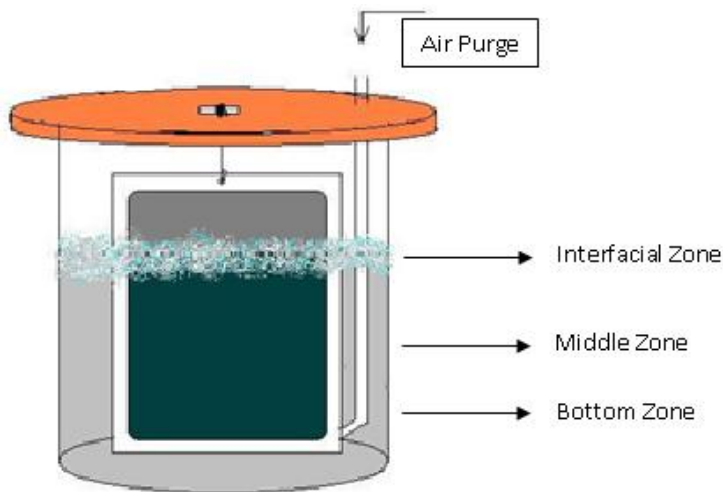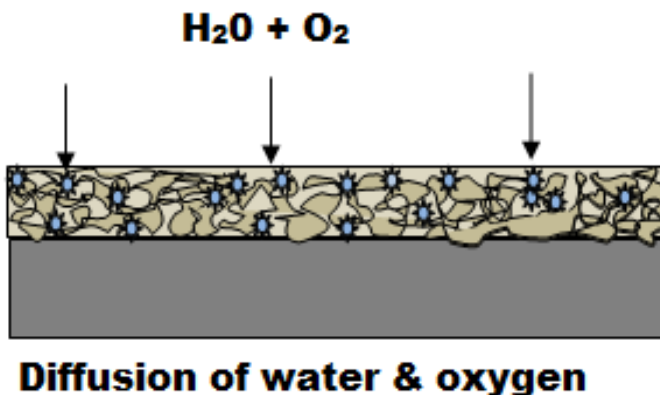
Figure 1. Panel immersed in aerated 3.5% NaCl.

Figure 2. Take up of aerated water by the paint film within incubation period.

material by Table 2.

Mechanism of paint film degradation

Incubation period

The incubation period is always required for the initiation of a blister on polymer–coated steel panels. For panels containing no apparent defects or small pores, the time taken by the blisters to nucleate is much longer than for panels containing defects [Robert et al., 1997; Chuang et al., 1999]. The water uptake by the polymer film is a function of degree of crosslinking and film thickness. In saline solutions the diffusion of ionic species through the film also depend on chain structure and length of diffusion path. High degree of crosslinking limit the approach of water and ions to the steel surface due to

tourteous path within the polymer film as depicted in Figure 2. The paint condition before immersion was as presented in Figure 3a. The absorption of water within the intrinsically defective paint film chain structure will cause a concentration gradient in the film for more water take up hence causing swelling as shown in Figure 3b. The initial 72 h delay in blister formation, when G02 painted surface was immersed in a water solution containing salt, the diffusion was gradual leading to film swelling with a volume expansion. The corrosion spots were appeared at surface of paint film which estimated according to ASTM D610 were close to rust grade 8-S (0.1% Rusted).

Blister nucleation/initiation

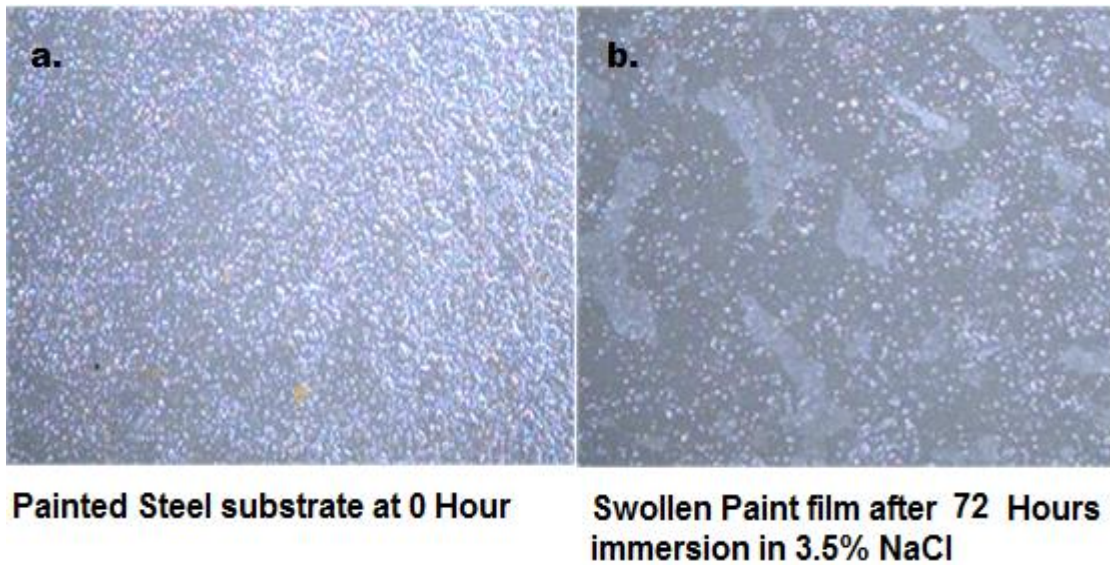The production of OH$^-$ ions at the cathodic regions of

Figure 3. G02 paint film surface condition at (a) 0 hour (b) 72 h.

Paint/metal interface by oxygen reduction reaction will generate osmotic pressure for the diffusion of cations. These anoins will increase H at the film/substrate interface. Thus the local accumulation of electolyte at the interface intiated blistering which is considered first indication of breakdown in the protective nature of paint film. Blisters form the local regions where the film lost its adhesion and water may accumulate at the delaminated sites hence initiate corrosion. The nucleation of blistering involves the following setps.

Built-up of osmotic pressure: The air saturated water absorption within the paint coating when reaches to its maximum caused swelling. Further diffusion of aerated water when reaches to the close proximity of metal paint interface, an osmotic pressure develops for more water to diffuse in. This pressure may develop due to the imperfection in paint metal bond (rusty surface), contamination level of metal surface, and surface free energy. Very strong adhesion may suppress corrosion by resisting the development of corrosion product, or water build-up under the coating [Patrick and Millar, 1962]. Also the driving force for osmotic blistering is the presence of soluble salt at the paint /substrate interface. Continous penetration of water through paint at the interface form 3.5% NaCl solution will built-up osmotic force accelerate the initiation of blisters within the paint coating. [9]. Steel corrodes very slowly in pure water, but with dissolved oxygen the ferrous ions and hydroxyl ions form ferrous hydroxide $Fe(OH)_2$ by following reactions.

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

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

$$Fe^{2+} 2OH^- \rightarrow Fe(OH)_2 \downarrow \tag{3}$$

The oxidation of steel surface (Equation 1) will occur at the center of blister initiation site and oxygen reduction reaction (Equation 2) will cocentrate at the periphry of blister.

Fe(OH)$_2$ has low solubility in water (0.0067 g/L at 20°C), thus precipitated at the site of corrosion and inhibited diffusion necessary to continue corrosion [Amy, 2006]. Hence blister of small size which do not grow formed. It was also observed durring exposure of painted samples that at micro-pores and defects sites the corrosion spots appeared.

Diffusion of ions: The formation of free micro passage ways within the paint film and formation of ferrous hydroxide at the metal paint interface at the nulceated blisters periphery attracted Na$^+$ and Cl$^-$ ions at the interface where these ions reacted with ferrous hydroxide in the following manner.

$$Fe(OH)_2 + [Na^+Cl^-]_{H2O} \rightarrow FeCl_{2(Soluble)} + NaOH \tag{4}$$
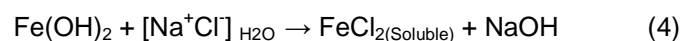
The formation of NaOH locally at the Blister initiation site increased the pH blister solution to 8. The Energy Despersive Spectroscopy (EDS) elemental analysis at the rust spot qualitatively validated the presence of Na$^+$ and Cl$^-$ ions in the spectrum as shown in Figure 4. The high intensity peaks of Cl$^-$ in EDS spectrum represented the domination of Cl$^-$ ions ingress at the paint/metal
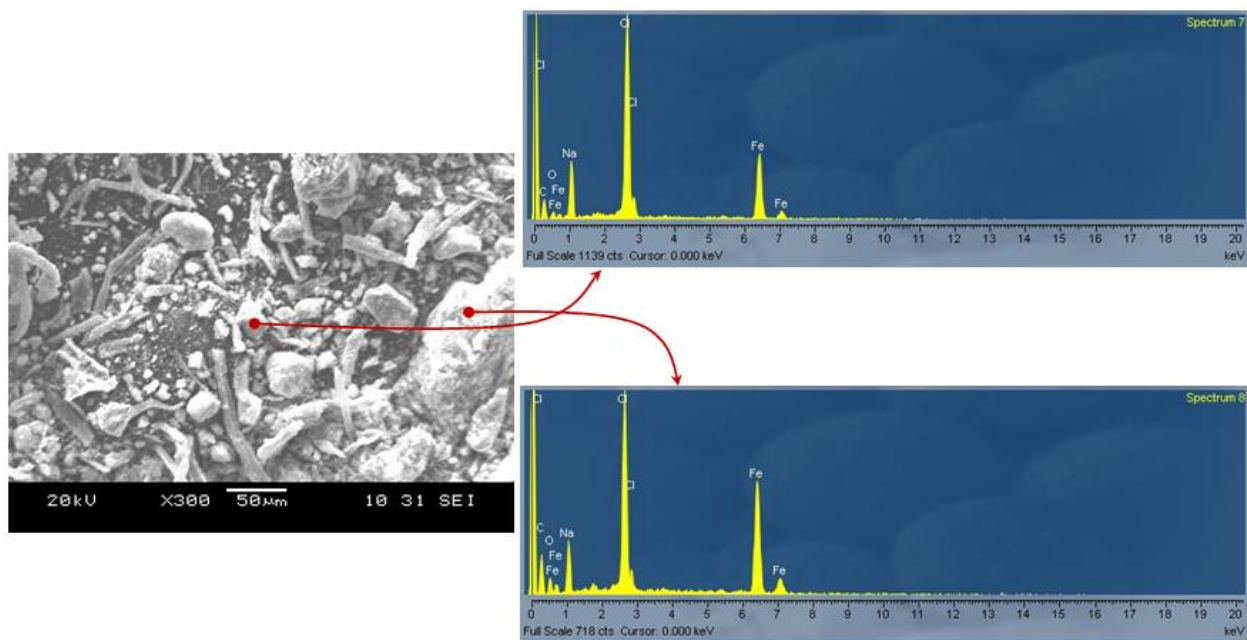
Figure 4. SEM, Energy dispersive spectroscopy elemental analysis.

interface than Na$^+$ ions.

Growth of blister

The cations such as Sodium Na$^+$ migrate through the paint micro passage ways to the cathodic areas where it forms NaOH. This developed local pH gradient between paint/metal interface and paint/solution interface. This may result in the transpotation of OH$^-$ away from the paint metal interface. Where as the anions Cl$^-$ migrate to the anodic areas where they will form FeCl$_2$ which is soluble in water and will diffuse away from the site of corrosion. As a result more water with dissolved oxygen diffuse in and produces more Fe^{2+} and OH$^-$ ions, which causes the blister to grow untill the cycle repeats again and again.This may be oxidized hydrolysed, and precipitated as a rust some distance away from the corrosion site. The stimulating Cl$^-$ anions if do not arrested may re-enter the corrosion cycle untill it becomes physically locked up in insoluble corrosion products [Amy, 2006; Kreislova and Geiplova, 2012].

The bliser will continue to grow untill the corrosion cycle stops due to the formation complex corrosion product and arrested the Cl$^-$ and Na$^+$ ions.

EFFECT OF SURFACE MORPHOLOGY ON PAINT DEGRADATION MECHANISM

Depending upon the surface profile the mechanism of paint delamination was a function of surface roughness. It was observed through exposure of painted steel panels in saline solution that grit blasted sample G02 by Grade 17 grit produced higher surface roughness (5.42 µm) and presented least cathodic blistering phenomenon as compared to the ground (G01) and G03 grit blasted with finer grit Size Grade-20.

The pictorial view of blister growth when painted steel panels were exposed to artificial sea water is shown in Figure 5 to 7 for 120, 240 and 480 h respectively.

The pictorial data of samples G01, G02 and G03 is provided in Tables 3 to 5 respectively for the evaluation of blister size, frequency and rust grades by following ASTM D-714 and ASTM D-610 respectively. It was evaluated from data that the blister growth rate was higher for G01 and G03 due to comparitively least surface area available for uniform adhesion to the steel surface than the rougher surface of G02. It was therfore very few blister having size 10 and rust grade 6 evan after 120 h at the bottom zone of panel. The detail of paint surface blister and rusting grades at the bottom, middle and interfacial zones of panel may be pridicted from these tables.
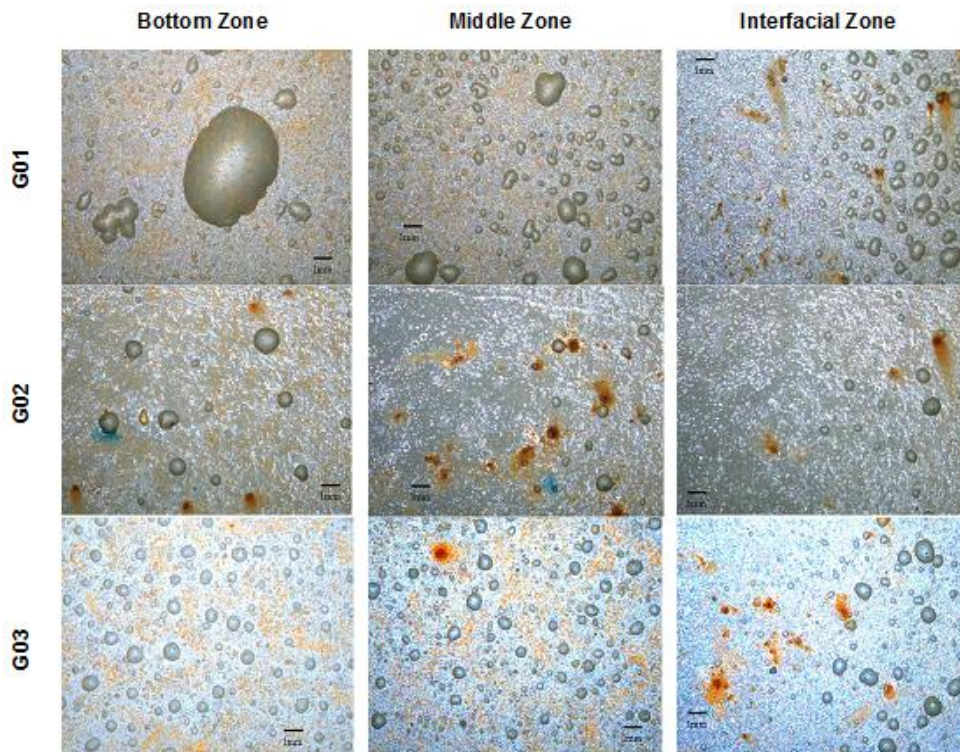
Conclusion

The nature of surface will determine the paint film integrity with respect to coating adhesion, disbondment rate and substrate anticorrosive property. The degradation mechanism is devised for paint film deterioration during its exposure to saline (3.5% NaCl)
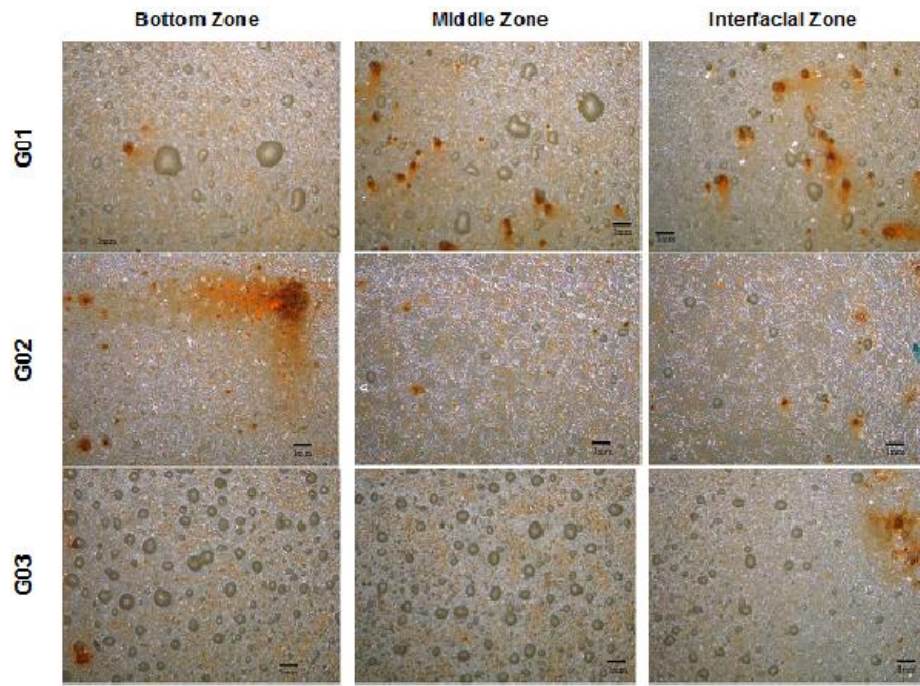
Figure 5. Stereo-micrographs of blister formation after 120 h immersion.

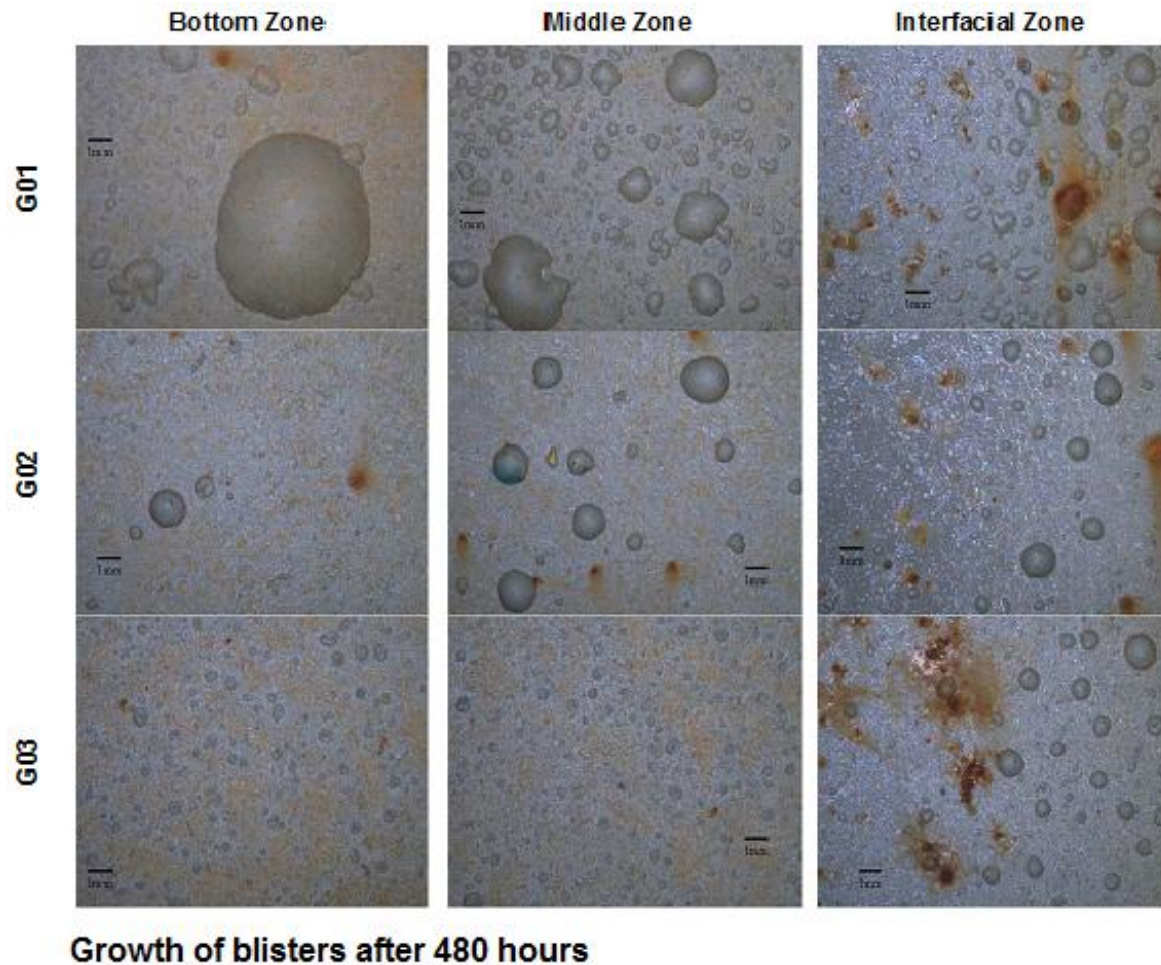**Figure 6.** Stereo-Micrographs of painted surfaces after 240 h.

Figure 7. Stereo-micrographs of painted samples after 480 h.

Table 3. Pictorial data of painted samples G01.

Exposure			ASTM Blister size and frequency at different zones			
Sample ID	Time (h)	ASTM designation	Bottom zone	Middle zone	Interfacial zone	Description
G01	0	Size	10	10	10	Incubation period
		Frequency	Nil	Nil	Nil	
	240	Size	4	2	2	Relatively small size blisters at the bottom zone due to the formation of few larger blisters
		Frequency	MD	MD	MD	
	480	Size	2	2	2	Blisters size remained same but increase in blisters density at the bottom and middle zones
		Frequency	D	D	MD	

solution. The lead based epoxy paint coating on ground (G01) and grit blasted (G03) did not show deterioration in initial incubation period of 72 h as compared to G03 whose incubation period was extended to 120 h. The degradation started by swelling of paint coating followed by nucleation of blisters. The osmotic pressure built up by

Table 4. Pictorial data of painted sample G02.

Exposure			ASTM Blister size and frequency at different zones			
Sample ID	Time (h)	ASTM designation	Bottom zone	Middle zone	Interfacial zone	Description
	0	Size	10	10	10	Incubation period
		Frequency	Nil	Nil	Nil	
G02	240	Size	Rust grade 4	2	2*	Few blisters were seen at middle zone was 10% rusted with no blister and interfacial zone was 16% rust with
		Frequency	10%	F	M**	
	480	Size	Rust grade 1	2	2*	Blisters size remained same but increase in blisters density at the bottom and middle zones
		Frequency	50%	M	M**	

*Blistering + Rusting; **Medium blister density (M) + approximately one sixth of the surface rusted.

Table 5. Pictorial data of painted sample G03.

Exposure			ASTM blister size and frequency at different zones			
Sample ID	Time (h)	ASTM designation	Bottom zone	Middle zone	Interfacial zone	Description
	120	Size	4	4	4*	Incubation period
		Frequency	D	D	M	
G03	240	Size	2	2	2	Blisters at bottom and middle zone grew and rust grade 6-S (1% rusted at the middle and rust grade 5-G (3% rusted) at
		Frequency	MD	MD	M	
	480	Size	2	2	2**	Blisters size remained same but Rupturing of blisters at the bottom and middle zones took place
		Frequency	D	D	MD	

*Rust grade 6-S, 1% rust; **Rust grade 4-G, 10% rusted.

the concentration gradient development in small blisters accelerated oxygen reduction reaction at the periphery of nucleated blister with a synergistic oxidation reaction at the center. These localized reactions resulted in the growth of blisters by delaminating paint at the interface. As compared to G01 and G03 the growth of blister was limited in G02 due to higher surface roughness and relatively better adhesion of paint coating with the steel surface. It was concluded that higher the surface roughness greater would be the degradation resistance in saline solutions.

REFERENCES

Amy F (2006). "Corrosion control through organic coatings" CRC press Tylor and Francis group, ISBN 0-8493-7278-X, 2006.

B.del A, Veleva L, Di Sarli AR, Elsner CI (2004). Progress in organic coatings, 50: 179-192.

Castle JE, Watts JF (1985). Interface chemistry of stoved organic coatings Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 361.

Chuang TJ, Nguyen T, Lee S (1999). "Micro-mechanic model for cathodic blister growth in painted steel", The journal of Coatings Technology, August 1st 1999.

Doherty M, Sykes JM (2008). "A quantitative study of blister growth on lacquered food cans by scanning acoustic microscopy", Corrosion Sci., 50: 2755-2772.

Kreislova K, Geiplova H (2012). "Evaluation of Corrosion Protection of Steel Bridges", Procedia Engineering, 40: 229–234.

Leng A, Streckel H, Hofmann K, Stratmann M (1999).

The delamination of polymeric coatings from steel Part 3: Effect of the oxygen partial pressure on the delamination reaction and current distribution at the metal/polymer interface Corrosion Sci., 41: 599.

Nelson F, de-Oca GM, Colas R (2012). "Lack of adhesion of paint in galvanised steel strip" Engineering Failure Analysis, December 2012, 26: 175–181.

Patrick RL, Millar RL (1962). "Handbook of adhesives", Skeist, I., Ed. Reinhold Publishing Corp., New York, 1962, p. 602.

Robert B, Debbie M, Chuck M, Tom H, Jeff B, Ernestine M (1997). Why surface preparation is important J. Protective coatings Linings (sep 1997), Pp 61-64.