

The Role of Interfacial Layers on the Performance of an Epoxy/Polyester Powder Coated Aluminium Alloy

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ABSTRACT

The influence of polyacrylic acid (PAA) and a blend of polyacrylic acid with hexafluorozirconic acid treatments on the performance of an epoxy/polyester powder coating on a 1050 Al substrate has been studied and compared to the performance of the same system using a so-called chromate/phosphate conversion coating. The chemical interactions between pretreatments and Al substrates were examined using FTIR spectroscopy and various accelerated test methods were also employed. Two mechanical adhesion measurement methods were used under wet and dry conditions, namely a vertical pull-off test in the dry state and the tape test under dry and wet conditions. The water permeation of the differently pretreated powder coated samples was studied using a capacitance measurement method. FTIR results showed two modes of interaction; namely ionic and complex formation between COO^- and Al^{3+} . Various experiments revealed that PAA improved only the dry adhesion but as a standing alone treatment it did not provide an overall improvement in anti-corrosive performance. The water uptake measurements proved that pretreatment does not considerably affect the properties of the coatings during water permeation stage. The use of various techniques revealed that relatively good performance of the powder coating is due to a high ohmic resistance of the coating prior to and after saturation with water, reasonably low water solubility and good adhesion to the substrate.

Key Words: aluminium, pretreatment, powder coating, corrosion, polyacrylic acid

INTRODUCTION

Aluminium and its alloys are widely used because of

their properties, such as lightness in weight and relatively good corrosion resistance, in addition to non-toxic qualities [1].

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Although aluminium naturally supports an air-formed film, about 2–3 nm in thickness, it is an insufficient barrier for relatively long-term corrosion prevention of the underlying Al. Passivated aluminium is attacked in certain environments, even when it is coated with an organic coating providing additional corrosion protection and localized corrosion may occur [2].

Consequently, chemical conversion coatings are applied to the aluminium surfaces in order to improve their corrosion resistance and/or establish a base for subsequent application of organic coatings (i.e., paints). Conversion coating of aluminium and its alloys is generally performed in solutions containing chromate and fluoride ions [1]. Such a coating usually develops in the presence of fluoride species, and is supported by cathodic reduction of Cr (VI) to Cr (III) species and hydrogen evolution. Chromium-based treatments have been used widely with good anti-corrosive performance, but the toxicity and carcinogenic nature of hexavalent chromium are well documented [3]. Many alternative treatments, including zirconium- or titanium-containing processes, or thin layers of polymeric materials, have been introduced as substitute for chromium-based pretreatments [1, 4–11].

Since the aluminium surface and PAA are hydrophilic in nature [8, 9], it is predicted that chemical interaction may take place between this pretreatment and aluminium oxides film over the substrate surface. In recent years, many studies [4–11] have investigated the performance of PAA treated metal oxides. It is concluded that oxides of divalent metals react more readily than oxides of trivalent metals. Therefore, aluminium oxide reacts relatively slowly compared to divalent metal oxides, and the reaction rates are not influenced by temperature variation. According to these results the reaction rate is proportional to the pH values of the metal oxides.

Thus, the pH values for CaO, ZnO, CuO, Al₂O₃ and Cr₂O₃ are 12.7, 9.4, 8.1, 8.0 and 7.9, respectively, and the reaction rates of PAA with the various metal oxides decreases in the order CaO > ZnO > CuO > Al₂O₃ > Cr₂O₃.

However, despite the previous findings, there is

no clear mechanism for the role of PAA as a surface treatment prior to powder coating. In order to assess the performance of the powder coated aluminium sample, supporting an air-formed oxide [1], particular attention has been paid to pretreatments prior to the powder coating application based on the polymeric materials.

Chemical interactions have been probed by FTIR, with performance and durability assessed by various standard tests and electrochemical measurements (EIS). However, PAA is shown to improve only dry adhesion but as a standing alone pretreatment did not provide overall improvements in anti-corrosive performance.

Therefore, hexafluorozirconic acid (PAAZR) treatment was selected, as a further alternative to the chromate/phosphate conversion coating (CPCC) based pretreatments.

Water Permeability of the Coatings

The water permeation in the coating film also can be determined by the increase of the coating capacitance [12–14]. The dielectric constants of organic coatings and water are about 4–8 and 80, respectively at ambient temperatures [13]. Therefore, the permeation of a small amount of water through the coating, can contribute to a relatively large change in the coating capacitance. It is necessary to determine the capacitance of coating in its dry condition (C_0), with the capacitance calculated from the following expression [12–14]:

$$C_c = \frac{\epsilon_0 \cdot \epsilon \cdot A}{d} \quad (1)$$

where, C_c is the coating capacitance, ϵ_0 is permittivity of vacuum (8.85×10^{-12} F/m), ϵ is the dielectric constant of the coating, A is the exposed area and d is the coating thickness.

The transport of a gas or vapour through a coating depends both on its solubility within the coating matrix and its ability to diffuse through that matrix. Solubility, S (kg/m^3 or %), is the maximum amount of water that may permeate through the coating. Further, it is assumed that no swelling occurs.

Therefore:

$$S = \frac{V_w}{V_c + V_w} \quad (2)$$

where, V_w is water volume (permeated) and V_c is the coating volume (dry). Alternatively, the volume fraction of penetrated water, ϕ_0 , is given by:

$$\phi_0 = \frac{V_w}{V_c + V_w} \approx \frac{V_w}{V_c} \text{ (kg/m}^3 \text{ or \%)} \quad (3)$$

The diffusion coefficient, D , expresses the mobility of water molecules in the coating. It is defined by the Fick's first law of diffusion, eqn (4), which is the rate at which species diffuse in a material. Fick's law is defined as the number of atoms passing through a plane of unit area in unit time.

$$J = -D \frac{\delta c}{\delta x} \quad (4)$$

Where, J is the rate of transfer per unit area of section, c is the local concentration of water in the coating and x is the directional distance, perpendicular to the substrate.

The permeation coefficient, P , of water in an organic coating gives an overall indication of the permeability of the coating, by combining S and D . Thus,

$$P = S \times D \times \rho$$

where, $\rho = 1 \text{ g/cm}^3$, thus: $P = S \times D$ (5)

In the case of permeation of water through a coating, the concentration gradient is not linear [13]. Water transports across the film and fills the free spaces within the coating matrix. Thus, the permeation of water leads to an accumulation of water in the coating, which may be described by Fick's second law of diffusion. Fick's second law describes the situation before the steady-state transfer rate is reached [15].

$$\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2} \quad (6)$$

Based on different solutions of Fick's second law, various methods have been used to calculate the diffusion coefficient of water into a coating on a

substrate¹⁵. In this study the $t_{0.5}$ method was used, which calculates D at time where the relative volume fraction ϕ_0/ϕ_s , equals one half.

$$D_{0.5} = \frac{0.04919 \cdot 4L^2}{t_{0.5}} \quad (7)$$

Where, $D_{0.5}$ is the diffusion coefficient, L is the coating thickness, ϕ_s is the volume fraction at saturation point and $t_{0.5}$ is time when $\phi_0/\phi_s=0.5$.

EXPERIMENTAL

Materials and Methods

Aluminium (1050) sheet, 0.5 mm thickness, was supplied by Arak Aluminium Co. Polyacrylic acid, PAA, (average molecular weight: 104,000) was supplied by ACROC (Fisher Chemicals) as a 25 % solution in distilled water, and hexafluorozirconic acid, PAAZR, was obtained from Aldrich Chemicals Co. as a 45 % solution in distilled water.

Preliminary surface cleaning was performed in acetone using a soft brush. The samples were treated in one of the following solutions; (1) 0.5% PAA, (2) 1% PAA, (3) 2 % PAA, treated at $20 \pm 1^\circ \text{C}$ for 30 min, and (4) 0.1 % PAA + 0.1 % H_2ZrF_6 (PAAZR), (5) 0.1 % H_2ZrF_6 (ZR), treated at $20 \pm 1^\circ \text{C}$ for 30 s. For comparison, a CPCC solution was also used; the treatment involved the Alodine procedure [1], with a specific immersion time of 5 min.

A commercial epoxy/polyester hybrid powder coating (supplied by Mega Co., Ral 9016, and with trade name of White 123 for interior use) was applied to the pretreated aluminium samples using a 405 Stajet electrostatic spray gun. The powder-coated samples were then placed in an oven for about 15 min at 180°C to cure. The thickness of the cured powder coated samples was measured using an Elcometer 256 instrument with an accuracy of 0.1 μm . Measurements were carried out on a set of five different replicate samples; the powder coating thickness varied from 50.2 to 61.4 μm .

FTIR Spectroscopy

A Perkin Elmer FTIR spectrophotometer, (Spectrum

2000 model) was used. Pretreated aluminium surfaces (without powder coating) were analyzed in a reflection-absorbance spectroscopy attachment; to cover a range of PAA concentrations, specimens treated in 0.1–5% PAA were used, and 4 scans, with a resolution of 8 cm^{-1} , were analyzed. In order to detect the small peaks related to the carbonyl groups, it was necessary to reduce the background water vapour by purging dry nitrogen gas into the sample and the detector areas.

Accelerated Tests

Three separate accelerated test methods (salt spray, full immersion and humidity exposure) were used. Treated samples (with and without powder coating, and cross scribed in all cases) were placed in a standard salt spray chamber for 1000 h at $35 \pm 1.7\text{ }^\circ\text{C}$ (ASTM B117), immersed in distilled water for 7 days at $38 \pm 2\text{ }^\circ\text{C}$ (ASTM D870) and exposed in a humidity cabinet for 1000 h at $38 \pm 2\text{ }^\circ\text{C}$ (ASTM D 2247). Visual assessments of the macroscopic surface and the scribed regions were performed at different time intervals.

Adhesion Measurements

The pull-off method was employed for the adhesion measurement [16]. The studs, 25.4 mm in diameter, were glued to the surface of the coated panels with a cyanoacrylate adhesive. After the adhesive had cured, the fixture was loaded and the joint was strained by a rate of 5 mm/min with an Instron machine (Universal Testing Instrument) until a plug of the powder coating material had detached from the substrate surface. For each test, seven replicate samples were employed, and the average value quoted. Additionally, tape adhesion measurements were undertaken immediately after salt spray and full immersion tests (wet adhesion). This involved scoring through the coating in a grid pattern. Thus six, approximately parallel, score lines were made, with a separation of 1.0 mm; a further six score lines were made perpendicular to the original score lines. For individual specimens, 25 grids were generated. Adhesive tape was placed on the grids, using a rubber eraser; the tape was then removed with a firm, steady pulling action.

Water Uptake Measurement

Capacitance measurements were used to monitor the water permeation through the coating.

Linear extrapolation of the coating capacitance versus \sqrt{t} to time=0 was employed to determine the coating capacitance at time=0 (dry condition) [13]. In order to calculate the coating capacitance values, electrochemical impedance spectroscopy (EIS) was performed on the powder-coated samples [17–19]. Then, the water uptake of the coating was determined using the Brasher and Kingsbury equation [10]:

$$X = \frac{\text{Log}(C_t/C_0)}{\text{Log}\epsilon_w} \longrightarrow X = \frac{\text{log}(C_t/C_0)}{\text{log } 80} \quad (8)$$

where, X is the percentage water uptake, C_t is the coating capacitance at time t , C_0 is the coating capacitance at time 0 and ϵ_w is the dielectric constant of water (80 at $20\text{ }^\circ\text{C}$). Linear extrapolation of the coating capacitance versus \sqrt{t} to time=0 was employed to determine the dry coating capacitance [12].

RESULTS AND DISCUSSION

FTIR

Figure 1 shows the Fourier transform infrared (FTIR) spectra of degreased aluminium and the 0.1% and 5% PAA treated aluminium substrates. The spectrum for the 5% PAA treated substrate displays the bands recorded in Table 1, which are also used as reference.

Degreased Sample

For degreased aluminium, the following bands were

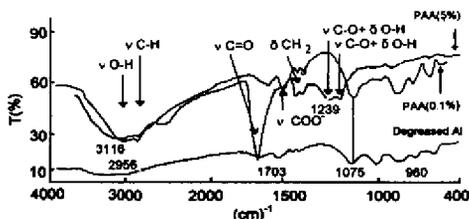


Figure 1. FTIR spectra of degreased, 0.1% and 5% PAA treated substrates.

Table 1. FTIR assignments for 1050 aluminium immersed in 5% PAA [7].

Wave number (cm ⁻¹)	Vibration mode	Functionality
3300–2200 very broad and intense	ν_{O-H}	OH (acid)
3000–2850	ν_{C-H}	CH (aliphatic)
1725–1700	$\nu_{C=O}$	COO (acid)
1558 (weak)	ν_{aCOO^-}	Acid salt
1550	$C_{OO^-, H}$	ionized form
1452	δ_{CH_2}	CH ₂
1416	$\delta_{HC(CO)}$	CH–CO
1239	$\nu_{C-O} + \delta_{O-H}$	OC–O–H (dimer)
1169	$\delta_{O-H} + \nu_{C-O}$	OC–O–H (dimer)
1090 (weak)	–OH	Adsorbed water
803	Unassigned	Unassigned

observed in the spectrum. A very broad band at 3300–2600 cm⁻¹ and a band at 1540 cm⁻¹, corresponding to OH groups (physically absorbed and bonded). The band at 960 cm⁻¹ corresponds to the bending modes in the aluminium oxide film and the band at 1075 cm⁻¹ is related to aluminium oxyhydroxide (pseudoboehmite film) [20].

5% PAA Treated Sample

Table 1 shows the bands and their related functionality for the 5% PAA treated aluminium sample. The broad band 3300–2200 cm⁻¹ corresponds to the OH groups. The bands at 1705 and 1725 cm⁻¹ are characteristic of C=O stretching modes for the protonated carboxylate groups, which form cyclic dimers and sideways chains, respectively [5]. The spectrum also reveals the presence of the ionized form (1550 cm⁻¹), characteristic of acid–base interaction between COOH groups of PAA with OH groups of aluminium oxide [6–7, 10,11].

0.1 % PAA Treated Sample

The characteristic carboxyl groups (COOH) were shifted from 1703 cm⁻¹ to 1550–1610 cm⁻¹ and 1300–1400 cm⁻¹ regions, which correspond to the asymmetric and symmetric C–O stretching modes, respec-

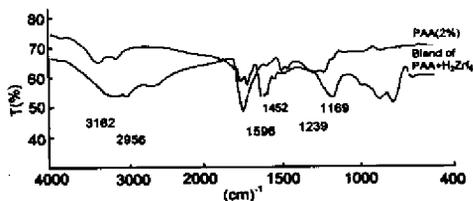


Figure 2. FTIR spectra of aluminium samples treated with PAAZR and 2% PAA.

tively, for COO⁻ ions [5]. The intensity of the band at 1705 cm⁻¹ also decreased compared with the 5% PAA FTIR spectrum. In addition, the double band at 1238 cm⁻¹ and 1169 cm⁻¹ in the 5% PAA spectra disappeared. This indicates that the dimer structure was not detected at the surface.

PAAZR Treated Sample

Figure 2 shows the FTIR spectra of aluminium sample treated with a PAAZR compound. As revealed in the Figure, the characteristic-stretch band of the carbonyl group at 1703 cm⁻¹ (COOH, C=O stretch, dimer), 1239cm⁻¹ (C–O stretch) and 1075 cm⁻¹ (OH bend) appeared from the spectra of the blended product. Deck et al. [11] suggested that disappearance of these peaks occur when acrylic acid reacts to form acrylate.

Accelerated Tests Analyses

The conventional 5 % NaCl fog chamber tests for pretreated samples (without powder coating) showed excessive corrosion and pitting within a few days on all PAA treated aluminium samples.

In contrast, CPCC and PAAZR treated samples were almost unchanged with no visible defects such as pits. Only degreased samples showed a better performance than PAA treated samples, even after 1000 h exposure.

For scribed powder coated samples, after a few days, blisters were observed with diameters of 0.5 to 1.0 mm, close to the scribed lines on the PAA treated specimens. Blister growth continued for PAA treated and degreased samples until the completion of the test. CPCC and PAAZR treated samples showed no visible change after completion of the test, even

Table 2. Pull-off test results.

Pretreatment	Adhesion strength (kg/cm ²)	Standard deviation
Degreased	84	13.75
Etched	91	11.90
Desmatted	88	8.81
CPCC	156	13.25
PAA (0.5 %)	115	14.98
PAA (1.0 %)	121	16.84
PAA (2.0 %)	108	13.22
PAAZR	122	17.8
ZR	116	16.6

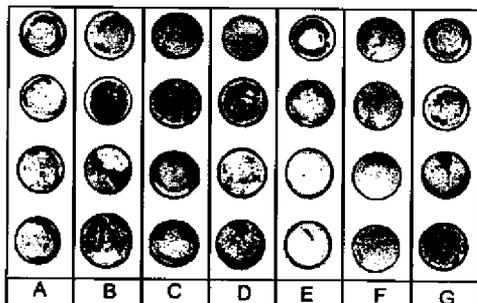
within the scribed regions.

Adhesion Measurements

Adhesion measurements contribute notably to a better understanding of corrosion protection with coatings and such phenomena as formation of blisters and under film corrosion are here readily detectable.

Pull-off Test

Visual observation of powder coated aluminium samples with different pretreatments after vertical pull-off test is shown in Figure 3. In this Figure, dark areas represent detachment of the powder coating (adhesive failure) from the substrate (metal surface) and the bright (or white) areas represent the adhesive



(A) Degreased; (B) PAA; (C) Etched; (D) Desmatted; (E) CPCC; (F) PZR; (G) ZR

Figure 3. Visual observation of powder coated aluminium samples with different pretreatments after vertical pull-off test.

failure at the adhesive /coating interface or/and cohesive failure within the powder coating. With the data of Table 2 and Figure 3, it is evident that, in the adhesive failures when adhesive strength was good. Possibly, cohesive failures occur in a weak boundary layer adjoining the interface (not completely cured regions or within a defective area). The results also show that the strengths of CPCC treated samples have an average value of 155 kg/cm², with the chromate layer having a significant influence on the initial strength.

PAA, PAAZR and ZR treatments increased dry adhesion compared with degreased, etched and desmatted specimens, indicating [18] that chemical interactions may proceed between PAA and/or PAAZR and the oxide surface.

Several interactions may take place between interfacial layers and the powder coating materials. It is thought that the following chemical interactions are more likely to take place between PAA based components and the epoxy/polyester powder coating material;

- Ring opening of the unreacted epoxy groups with the acidic groups in the PAA polymeric chain, leading to the formation of the hydroxyl ester.
- Esterification between the acidic groups in the PAA polymeric chain and the hydroxyl group formed in the powder coating network.
- Hydrogen bonding between hydroxyl groups in the PAA polymeric chain and the hydroxyl groups in the powder-coating network.
- Condensation esterification between the carboxylic acid groups in the powder coating network and the acidic groups in the PAA polymeric chain.

Tape Tests

Dry Condition: In the dry state, all powder-coated specimens had shown good adhesive strength. No failed squares were observed on the specimens. However, it is clear that the adhesive strength of the coatings in the dry state is less important to the corrosion performance of the coating [21] than the adhesive strength in the presence of water and corrosion products.

Wet Condition: In the wet state, powder-coated speci-

Table 3. Percentage adhesive remaining after the tape test.

Pretreatment	After salt spray Test	After full immersion test
CPCC	98.4	99.2
Degreased	93.6	95.2
PAA (0.5 %)	80.0	65.2
PAA (1.0 %)	92.0	87.0
PAA (2.0 %)	67.2	54.8
PAAZR	94.4	97.2
ZR	89.6	94.4

mens with different pretreatments showed different adhesive strengths. Powder coated specimens with CPCC and PAAZR pretreatment showed better adhesive strength than the other powder-coated specimens. The adhesive strength may be semi-quantified by using the following expression:

$$\text{Adhesive loss (\%)} = \frac{X}{25} \times 100 \quad (9)$$

Where, X is the average number of squares of detached coating.

The results of 5 individual wet adhesion measurements are shown in Table 3, which reveals that the adhesive remaining on PAA treated samples was less than that of CPCC and degreased samples. PAA is water-sensitive [17] therefore, when aluminium surfaces, on which PAA was deposited, are exposed to aqueous environments dissolution may proceed, leaving little ionic or complex interaction with the metal surface.

Water Uptake

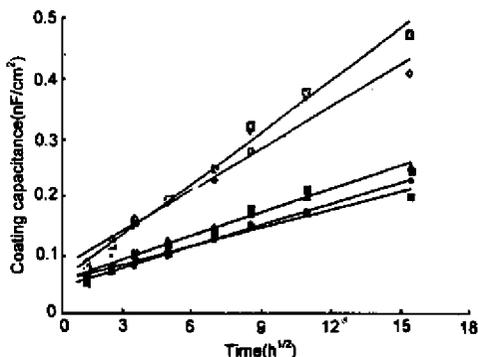
The coating capacitance values increase during the initial period of immersion because of water uptake, after which period the capacitance remains almost constant (saturation of the coating layer with water) and after 20 days, they start to increase further. This may be because; water may accumulate under the coating film.

Figure 4 reveals the linear extrapolation of C_0 to time=0 for the powder coated aluminium substrates with different pretreatments. The calculated of the water permeability of the powder-coated samples are

summarized in Figure 5 and Table 4. In this Table, the material constants describing the water permeability parameters are listed as a function of different pretreatments. It is evident that the water permeability of the selected powder coated samples does not vary widely. During the permeation stage (first few days of immersion), pretreatment does not affect the water uptake of coatings and water uptake is an independent phenomenon. Powder coated aluminium samples reveal a lower amount of water solubility, ($S = 0.4\%$) compared to liquid based coating; as a result, there was little water available for condensation at the site of the blister. Thus, the relatively good resistance to blister growing may be due to low water solubility of the powder coatings.

Two factors may affect the water permeation through the coating [17]. These are the crystallinity and the chain stiffness of the film; these both decrease the diffusion rate as they increase. The diffusion rate for penetrating molecules decreases as the cross-linking increases. However, because of the absence of solvent in the powder coating formulation (more dense after curing) and possibly more cross-linking degree [17], the value of water permeation is relatively low.

Based on the results obtained from Figure 5 and



(□) Degreased; (△) PPA (5%); (◇) PPA (10%); (○) PPA (20%); (■) PZR; (●) Zr; (○) CPCC; — Linear (Degreased); — Linear (PPA 5%); — Linear (PPA 10%); — Linear (PPA 20%); — Linear (PZR); — Linear (Zr); — Linear (CPCC)

Figure 4. The coating capacitance as a function of \sqrt{t} for powder coated samples with different pretreatments during 20 days of immersion in 3 % NaCl solution.

Table 4. Water uptake, diffusion coefficient and permeability calculated from the capacitance measurements for epoxy/polyester powder coating with different pretreatments.

Pretreatment	Thickness (μm)	Water uptake S (V%)	Diffusion coefficient $D_{0.5}$ (m^2/s)	Permeability P ($\mu\text{g}/\text{m}\cdot\text{s}$)
Degreased	55.2	0.43	1.18×10^{-13}	0.051
CPCC	50.2	0.39	1.06×10^{-13}	0.042
PAA (5 g/L)	51.2	0.44	1.21×10^{-13}	0.053
PAA (10 g/L)	54.8	0.41	1.07×10^{-13}	0.045
PAA (20 g/L)	56.3	0.46	1.05×10^{-13}	0.051
PAAZR	60.1	0.40	1.19×10^{-13}	0.048
ZR	61.4	0.42	1.24×10^{-13}	0.052

literature [13], it appears that there are three different stages for the increase of coating capacitance and percent water uptake.

- First day of immersion: the water absorption was fast, between 0.15 to 0.26 %. This may be interpreted as the tendency of coatings to take water from columns perpendicular to the surface [14].

- In the second stage (1-5 days), the coating film takes up more water (about 0.13 %), the rate of water permeation however decreased. At this stage, the first sign of saturation was observed as the coating has a limited free diffusion thickness [12].

- Finally, in the third stage, the coatings were fully saturated with water. In some samples (e.g. PAA treated), a further increase was observed. This may be attributed to the clustering of water in, or under, the coating film [13].

General Discussion

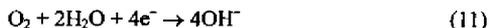
PAA Treated Samples

PAA treated samples revealed poor barrier properties, resulting in the hydration of aluminium oxide at the water-rich interface [22], with water being replaced by aluminium hydroxide and PAA-oxide bonds. In the absence of chloride ions, the main reaction at the interface between Al and the coating is aluminium hydroxide growth.



It is suggested that hydrated aluminium oxide decreases the stability of the adhesive joint in the

presence of water [23]. The coating layer may detach from the metal substrates at the metal/coating interface due to diffusion of both water and oxygen through the coating. Water penetrates through the coating with time, and reaches the coating/metal interface. It may solvate PAA molecules, resulting in a loss of adhesion. In addition, there is a cathodic reaction, eqn (11), occurring at the chemical impurities in the aluminium (residual flaws) surface



The high hydroxyl ion concentration dissolves the aluminium oxide and the aluminium metal and possibly attacks the polymer at the interface between the polymer and the substrate. With increasing immersion time, the radius of the high frequency semicircle dramatically decreased, suggesting that the barrier properties of the coating progressively decreased, and the corrosion rate continued to increase to the end of the test.

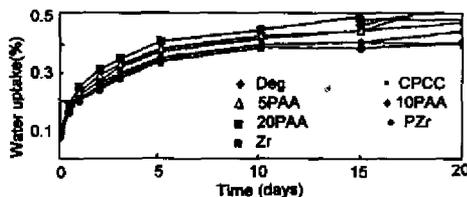


Figure 5. Water uptake of powder coated aluminium samples with different pretreatments during 20 days immersion in 3% NaCl solution.

CPCC Treated Samples

CPCC contains insoluble hydrated chromium phosphate [24], which may act as an efficient barrier to corrosion. Cr(VI) may be included in the conversion coating and is reduced at flaws [23] to Cr(III) to re-passivate any damaged surface. In the absence of pretreatment, the substrate is active and the resistance in situ is low when corrosion occurs. In the absence of a passive layer (CPCC) and the presence of under-film corrosion, the coating resistance is low because; there is an ionic current on the surface due to presence of anodic and cathodic sites, ionic migration within the film (electrolyte), local film changes and electro-osmotic movement of water [25].

PAAZR Treated Samples

ZR and PAAZR pretreated samples reveal good corrosion performance over the first 50 days of immersion in 3 % NaCl solution. It is proposed [10] that zirconium based treatment compounds, may protect the surface against corrosive environment, by inhibition of anodic reaction over the aluminium surfaces and as a result the passivity of the metal may increase. The mechanism of formation of zirconium-based pretreatments and producing pseudoboehmite film via boiling water treatment, are similar [26–28].

A further theory suggests that when a polymer is present in the conversion coating solution, it may act as a surfactant and modify the conversion coating. It is suggested [29] that PAA molecules assist in the production of a uniform conversion-coating layer on the metal surface. Another theory [11] suggests that the zirconium compound may act as a cross-linking agent for polymer network on the aluminium surface.

CONCLUSION

FTIR analyses suggest two possible chemical interaction modes between PAA molecules and the oxide coated macroscopic aluminium surface. The first is purely ionic, with chemical interaction between COO^- and Al^{3+} giving a band about 1550 cm^{-1} . The second is a complex formation, giving a

band in the 1600 cm^{-1} region.

PAA molecules are water sensitive, therefore, humidity or water may dissolve unreacted PAA molecules. After treating samples with water, there remains only a small amount of reacted molecules, in the form of an ionic bond or a complex interaction with the metal surface.

Relatively good performance of the powder coating is due to a high ohmic resistance of the coating prior to and after saturation with water, low water solubility of the coating itself and good adhesion of the coating to the substrate.

Although, polyacrylic acid improved the dry adhesion performance, it did not improve the overall anti-corrosion performance.

Accelerated tests and wet adhesion measurements showed that the degreased samples demonstrated a better performance than PAA treated samples. The CPCC treated samples gave the best performance and the PAAZR gave marginally second best performance in anti corrosive behaviour.

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