ACET AND EIS ASSESSMENT OF HIGH PERFORMANCE POWDER COATING DUPLEX SYSTEMS

Index

1. Introduction

2. Innovative approach to duplex systems

3. Objective

4. Materials

5. Results

6. Conclusions
1. Introduction
Corrosion: *Irreversible interfacial reaction of a material (metal, ceramic or polymer) with its environment resulting in its consumption* (IUPAC definition)

- Economic loss: 300.000M€ per year
- Reduction of service life
- Accidents (Part rupture)
- Economic loss: 300.000M€ per year
Corrosive protection of steel

Coatings

Metallic
Inorganic (Non-Metallic)

Organic

Liquid paint

Powder paint

1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions
Corrosive protection of steel

Coatings

- Metallic
- Inorganic (Non-Metallic)
  - Organic

Solvents

- Liquid paint
- Powder paint
Corrosive protection of steel

Coatings

- Metallic
- Inorganic (Non-Metallic)
- Organic

Solvents

- Liquid paint
- Powder paint

Combination of protective systems ➞ Duplex System

Coating

Galvanized steel

Corrosion protection is 1.5 to 2.5 times longer than the sum of the lifetimes of zinc and paint used individually.
2. Innovative approach in duplex systems
2. Innovation

- Elimination of pretreatment step
- Using high performance materials
- Optimization of formulation using innovative techniques
Elimination of pretreatment step

Coating system

Galvanized steel
Elimination of pretreatment step

Coating system

Galvanized steel

Pretreatment

Primer
Elimination of pretreatment step

Coating system

Galvanized steel

Pretreatment

Primer

↑Cost

Monolayer coating

Galvanized steel
Using high performance materials
Using high performance materials

Alkoxy groups

- OCH₃: Alkoxy groups. Form bonds with inorganic substrate, improves adhesion to the coating.

R: Non hydrolyzable organic group. Interacts with coating.
Using high performance materials

Alkoxy silanes → Adhesion promoters

R: Non hydrolyzable organic group. Interacts with coating.

-OCH₃: Alkoxy groups. Form bonds with inorganic substrate, improves adhesion to the coating.

Silica-supported
Using high performance materials

\[ \text{SiO}_2 \]
Using high performance materials

\[ \text{H}_3\text{CO} - \text{Si} - \text{OCH}_3 \quad \rightarrow \quad \text{HO-Si-OH} \quad \rightarrow \quad \text{HO-Si-O-Si-O-Si-OH} + \text{SiO}_2 \]

\[ \text{SiO}_2 \quad \rightarrow \quad \text{HO-Si-O-Si-O-Si-OH} \quad \leftarrow \quad \text{HO-Si-O-Si-O-Si-OH} \]
Using high performance materials


Using high performance materials
Using high performance materials

Anticorrosive pigments

Organophilized zinc phosphate molybdate
**Using high performance materials**

**Anticorrosive pigments** → **Organophilized zinc phosphate molybdate**

**1. Introduction**
**2. Innovation**
**3. Objective**
**4. Materials**
**5. Results**
**6. Conclusions**
|-----------------|---------------|--------------|--------------|------------|---------------|

Optimization of formulation using innovative techniques
Optimization of formulation using innovative techniques

Accelerated Cyclic Electrochemical Technique (ACET)
A sequence Stress / impedance is repeated several times.
Optimization of formulation using innovative techniques

ACET results in equivalent circuit

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>DEFINITION</th>
<th>EFFECTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{po}$</td>
<td>Pore Resistance</td>
<td>Degradation due to increased porosity</td>
</tr>
<tr>
<td>$C_c$</td>
<td>Coating capacitance</td>
<td>Water Absorption</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Polarization resistance</td>
<td>Corrosion in the interface</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>Double layer capacitance</td>
<td>Delamination</td>
</tr>
</tbody>
</table>
3. Objective
Development of powder monolayer coatings with high performance properties to protect galvanized steel from corrosion
4. Materials
Resin + Crosslinker

The diagram shows the reaction of Resin + Crosslinker to form a network structure. The structures on the left represent the components, and the right shows the resulting network.
Resin + Crosslinker + Additives

- Flow agent
- Degassing agent
- Waxes
- TiO₂
- Inorganic filler
Study 1

Resin + Crosslinker + Additives + Alkoxy silane

- Flow agent
- Degassing agent
- Waxes
- TiO₂
- Inorganic filler

Weight %

0
1
2.5
3.5
4.5
Resin + Crosslinker + Additives

- Flow agent
- Degassing agent
- Waxes
- TiO₂
- Inorganic filler

**Resin + Crosslinker** + **Additives** + **Anticorrosive Pigment**

- Flow agent
- Degassing agent
- Waxes
- TiO₂
- Inorganic filler

**Weight %**

0  1  2.5  10  15
Resin + Crosslinker + Additives

- Flow agent
- Degassing agent
- Waxes
- TiO₂
- Inorganic filler
Synergistic effect evaluation

Resin + Crosslinker + Additives + Alkoxy silane + pigment

- Flow agent
- Degassing agent
- Waxes
- TiO₂
- Inorganic filler
5. Results
Study 1. Alkoxysilane effect

ACET
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System with undeperformance
ACET
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System with high performance

System with undeperformance
Study 1. Alkoxysilane effect

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Reference (0% alkoxysilane)

System with undeperformance
Study 1. Alkoxysilane effect

ACET

UNE 48315:2011

1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions

System with underperformance

System with high performance

Reference (0% alkoxysilane)

2.5% alkoxysilane
ACET vs EIS

Study 1. Alkoxyisilane effect

1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions
Study 1. Alkoxy silane effect

ACET vs EIS

![Bode plots showing ACET vs EIS](image-url)
Study 1. Alkoxysilane effect

ACET vs EIS

Graphs showing the effect of alkoxysilane on ACET and EIS.

- Graphs for $R_p$ (Ω) and $C_{dl}$ (s/Ω) against % alkoxysilane for ACET (4th cycle) and EIS (1680 h).

Acronyms used:
- ACET
- EIS
- % alkoxysilane
- $R_p$ (Ω)
- $C_{dl}$ (s/Ω)
Study 1. Alkoxysilane effect

ACET vs EIS

- **$R_p$ (Ω)**
  - ACET (4th cycle)
  - EIS (1680 h)

- **$C_{dl}$ (s$^{0.5}$Ω$^{-0.5}$)**
  - ACET (4th cycle)
  - EIS (1680 h)

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1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions
Study 1. Alkoxyisilane effect

ADHESION TEST
UNE-EN 1465 (2009)

Substrates union by formulated systems and sequently cured (15 min, 180ºC)
Study 1. Alkoxy silane effect

Inverse impact resistance TEST

**UNE-EN ISO 6272-2:2002**

- Weight: 1kg
- Height: 1m

[Graph showing shear stress (MPa) for different concentrations: Ref, 1% A, 2,5% A, 3,5% A, 4,5% A]

- Poor adhesion
- Good adhesion
Study 1. Alkoxy silane effect

**Scanning Electron Microscopy (SEM)**

![SEM images of different concentrations of alkoxy silane](image)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Shear Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>4</td>
</tr>
<tr>
<td>1% A</td>
<td>5</td>
</tr>
<tr>
<td>2.5% A</td>
<td>6</td>
</tr>
<tr>
<td>3.5% A</td>
<td>7</td>
</tr>
<tr>
<td>4.5% A</td>
<td>4</td>
</tr>
</tbody>
</table>

Note: The bar chart shows the shear stress for different concentrations of alkoxy silane. The data indicates a significant effect of alkoxy silane on shear stress, with the highest concentration showing the highest shear stress.

>10µ

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*1. Introduction*  
*2. Innovation*  
*3. Objective*  
*4. Materials*  
*5. Results*  
*6. Conclusions*
**Study 1. Alkoxysilane effect**

## Salt Spray fog test

*EN ISO 12944*

<table>
<thead>
<tr>
<th>% Alkoxysilane</th>
<th>Exposure (h)</th>
<th>Failure mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (Ref)</td>
<td>430</td>
<td>DA</td>
</tr>
<tr>
<td>1</td>
<td>430</td>
<td>DA</td>
</tr>
<tr>
<td>2.5</td>
<td>430</td>
<td>DA</td>
</tr>
<tr>
<td>3.5</td>
<td>430</td>
<td>DA</td>
</tr>
<tr>
<td>4.5</td>
<td>430</td>
<td>DA</td>
</tr>
</tbody>
</table>

DA: Delaminated Area (>2 mm)  
B: Blistering

No differences: Delaminated Area failure occurs prior to Blistering failure
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Study 2. Anticorrosive pigment effect</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ACET
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System with underperformance

System with high performance

|Z| |Ω| Frequency (Hz)

Reference

10 % Pigment


Study 2. Anticorrosive pigment effect
ACET

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System with underperformance
Study 2. Anticorrosive pigment effect

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System with underperformance

System with high performance
1. Introduction  
2. Innovation  
3. Objective  
4. Materials  
5. Results  
6. Conclusions  

Study 2. Anticorrosive pigment effect

**ACET vs EIS**

Bode (4th cycle)  
Bode (1176 hours)
Study 2. Anticorrosive pigment effect

ACET vs EIS

- **$R_p$ (Ω)**
  - ACET vs EIS
  - % anticorrosive pigment

- **$C_c$ (s/Ω)**
  - ACET vs EIS
  - % anticorrosive pigment

- **$C_d$ (s/Ω)**
  - ACET vs EIS
  - % anticorrosive pigment

1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions
Study 2. Anticorrosive pigment effect

ACET vs EIS

1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions

- ACET
- EIS

- $R_p$ ($\Omega$)
- $C_c$ ($s/\Omega$)

- 10-15
# Study 2. Anticorrosive pigment effect

## Salt spray test

*EN ISO 12944*

<table>
<thead>
<tr>
<th>% Pigment</th>
<th>Exposure (h)</th>
<th>Failure mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (Ref)</td>
<td>430</td>
<td>DA</td>
</tr>
<tr>
<td>1</td>
<td>430</td>
<td>DA</td>
</tr>
<tr>
<td>2.5</td>
<td>430</td>
<td>DA</td>
</tr>
<tr>
<td>10</td>
<td>648</td>
<td>DA</td>
</tr>
<tr>
<td>15</td>
<td>648</td>
<td>DA</td>
</tr>
</tbody>
</table>

DA: Delaminated Area (>2 mm)
B: Blistering

Optimal between 10-15%
Study 1. Alkoxy silane Effect

2.5 % A
Study 1. Alkoxysilane Effect

Study 2. Anticorrosive Pigment Effect

2.5 % A

10 – 15% P
Study 1. Alkoxysilane Effect

Study 2. Anticorrosive Pigment Effect

Study 3. Combinated Systems:

<table>
<thead>
<tr>
<th>% Alkoxysilane</th>
<th>% Pigment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2.5</td>
<td>10</td>
</tr>
<tr>
<td>3.5</td>
<td>10</td>
</tr>
<tr>
<td>4.5</td>
<td>10</td>
</tr>
</tbody>
</table>
Study 3. Combined systems: Synergistic effect

ACET
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Reference

2.5 % alkoxysilane

10 % Pigment
1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions

Study 3. Combined systems: Synergistic effect

ACET

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2.5% alkoxysilane

1% alkoxysilane + 10% pigment
**ACET**

*UNE 48315:2011*

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**2.5 % alkoxysilane**

**10 % pigment**

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1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions

Study 3. Combinated systems: Synergistic effect
Study 3. Combined systems: Synergistic effect

ACET
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2.5 % alkoxysilane

1 % alkoxysilane + 10 % pigment

1 % alkoxysilane + 10 % pigment

10 % pigment
<table>
<thead>
<tr>
<th>Study 3. Combinated systems: Synergistic effect</th>
</tr>
</thead>
</table>
Study 3. Combinated systems: Synergistic effect

- $R_{\infty}$ (Ω)
- $R_p$ (Ω)
- $C_{C}$ ($s^n$Ω$^{-1}$)
- $C_{dl}$ ($s^n$/Ω)
Study 3. Combinated systems: Synergistic effect

**Graphs:**

- **Graph 1:**
  - Title: \( R_{\infty} (\Omega) \)
  - X-axis: Cycles
  - Y-axis: Log scale from \( 10^5 \) to \( 10^8 \)
  - Data points show two trends: Reference and % A Optimum.

- **Graph 2:**
  - Title: \( R_p (\Omega) \)
  - X-axis: Cycles
  - Y-axis: Log scale from \( 10^6 \) to \( 10^{12} \)
  - Data points show two trends: Reference and % A Optimum.

- **Graph 3:**
  - Title: \( C_C (s^n \ell_0) \)
  - X-axis: Cycles
  - Y-axis: Log scale from \( 10^{-9} \) to \( 10^{-6} \)
  - Data points show two trends: Reference and % A Optimum.

- **Graph 4:**
  - Title: \( C_{dl} (s^n \ell_2) \)
  - X-axis: Cycles
  - Y-axis: Log scale from \( 10^{-9} \) to \( 10^{-3} \)
  - Data points show two trends: Reference and % A Optimum.
Study 3. Combinated systems: Synergistic effect

- **$R_{\infty}$ (Ω)**
  - Reference
  - % A Optimum
  - % P Optimum

- **$R_p (\Omega)$**
  - Reference
  - % A Optimum
  - % P Optimum

- **$C_c (s^n,\Omega)$**
  - Reference
  - % A Optimum
  - % P Optimum

- **$C_{dl} (s^{n/2})$**
  - Reference
  - % A Optimum
  - % P Optimum
Study 3. Combinated systems: Synergistic effect

1. Introduction
2. Innovation
3. Objective
4. Materials
5. Results
6. Conclusions

- $R_{\infty}$ ($\Omega$)
- $R_p$ ($\Omega$)
- $C_c$ ($\mu F$)
- $C_{dl}$ ($\mu F$)
6. Conclusions
Monolayer powder coating has been developed to protect galvanized steel without pretreatment.

Alkoxy silanes improve anticorrosion performance due to the adhesion increase between the coating and the substrate.

Anticorrosive pigment inhibits corrosion mechanism due to its passivation action.

Improvement is shown combining the alkoxy silane and pigment effect in the systems (synergistic effect).

ACET technique optimize the evaluation of new coatings.
Acknowledgement: