AkzoNobel

MANCHESTER 1824
The University of Manchester

The effect of particles size distribution and cross-linking agent on the leaching behaviour of anti-corrosion species for long-term active corrosion protection on AA2024-T3 alloy

Ander Cervellera-Dominguez – AkzoNobel, Sassenheim, NED. School of Materials, The University of Manchester, UK
Peter Visser – AkzoNobel, Sassenheim, NED
Professor Xiaorong Zhou – School o Materials, The University of Manchester, UK
Simon Gibbon – AkzoNobel, Felling, UK

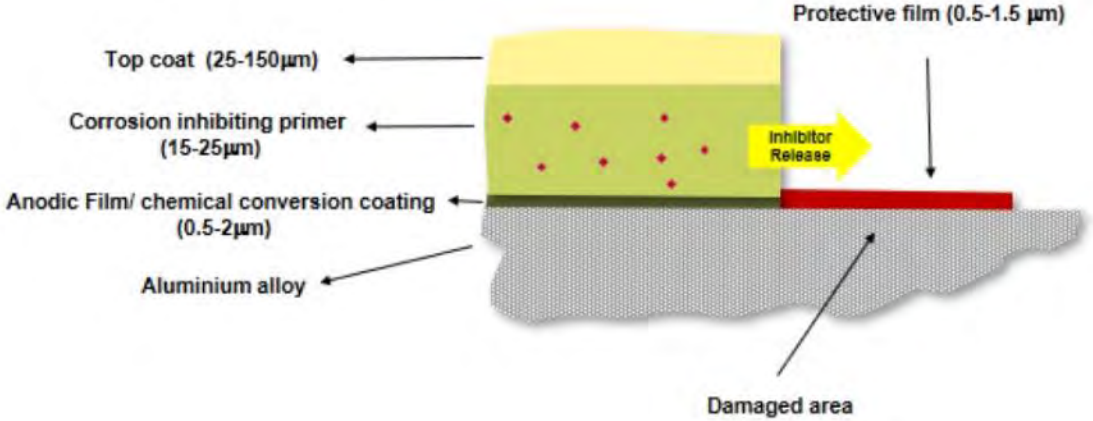
FFFC3 2020

SUSTICOAT
H2020-MSCA-ITN-2016/721451

Introduction

Active corrosion protection by organic coatings in aerospace

Organic coatings provide corrosion protection to aluminium alloy substrates



Active corrosion inhibition due to leaching mechanism

1. Moisture ingress and release of inhibitor
2. Transport and delivery of active species
3. Passivation of damaged area

- Criteria for corrosion inhibition via leaching

- Soluble inhibitor
- Fast and effective passivation mechanism
- Irreversible

H2020-MSCA-ITN-2016/721451

Introduction

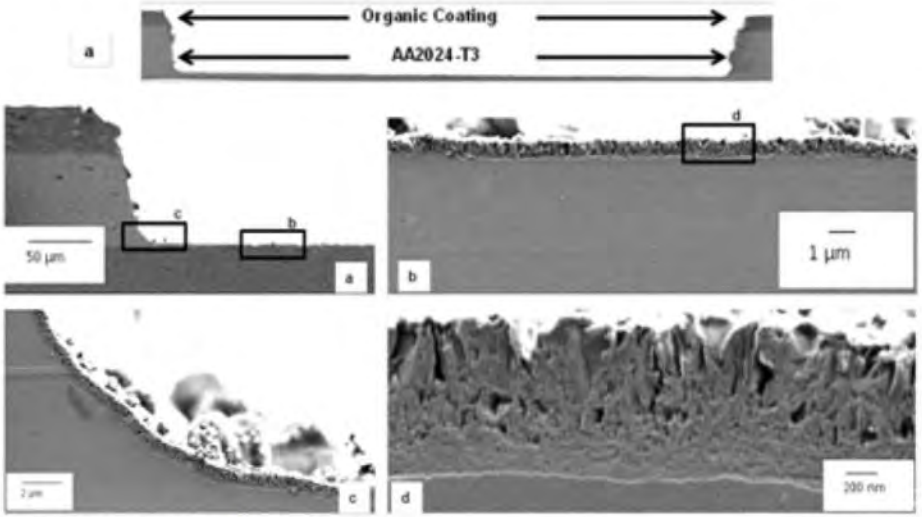
Corrosion protective properties of lithium leaching coating technology

Provide **fast**, **effective**, and **irreversible** corrosion inhibition

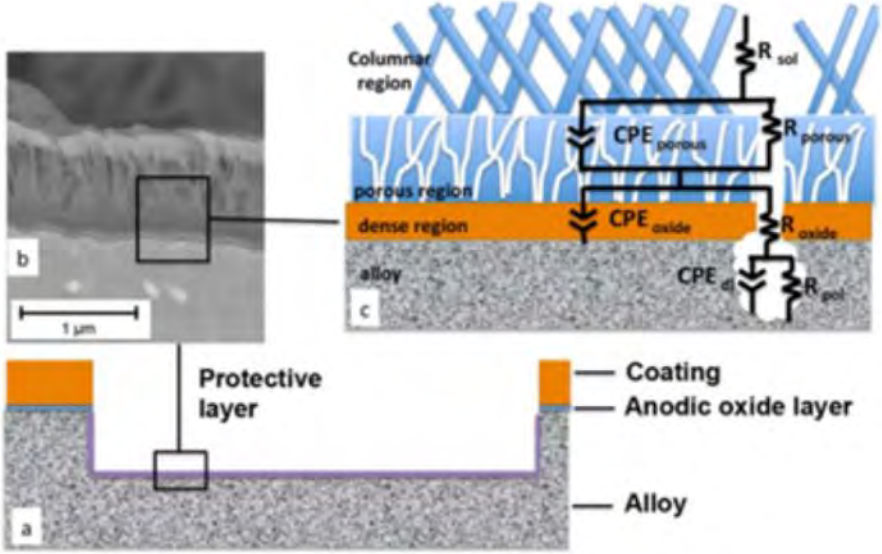
1. Leaching of lithium ions
2. Formation of a protective layer on the aluminium substrate

Relation of physical model with corrosion properties

- Oxide layer provides active corrosion protective properties



Visser et al. *Faraday Discuss.* **180**, 511-526 (2015)



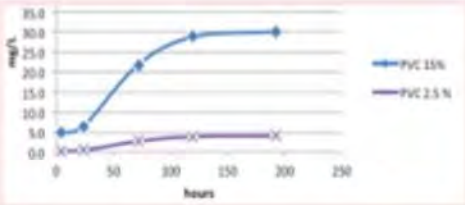
Visser et al. *Journal ofThe Electrochemical Society*, **164** (7) C396-C406 (2017)

H2020-MSCA-ITN-2016/721451

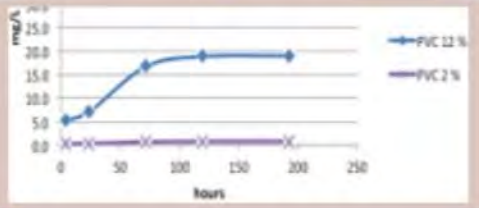
Introduction

The challenge of chromate replacement

	Strontium Chromate inhibition technology	Lithium leaching technology
Active Corrosion Protection	✓	✓
Solubility	0.12 g/0.1L ↓ 15 °C	1.36 g/0.1L ↑↑ 15 °C

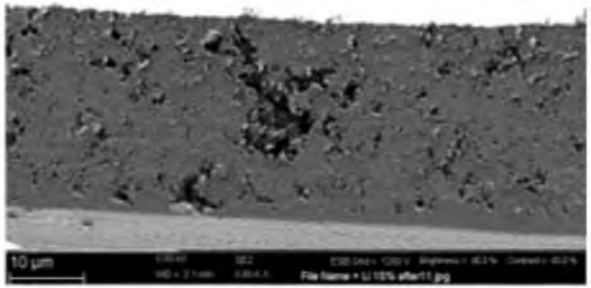


Lithium Carbonate



Strontium Chromate

The risks of using highly soluble inhibitors in organic coatings



- Risk of osmotic blistering
- Local dissolution of inhibitor
- Faster depletion of the inhibitor system

→

- Early failure of coating
- No corrosion protection
- Short service life of coating

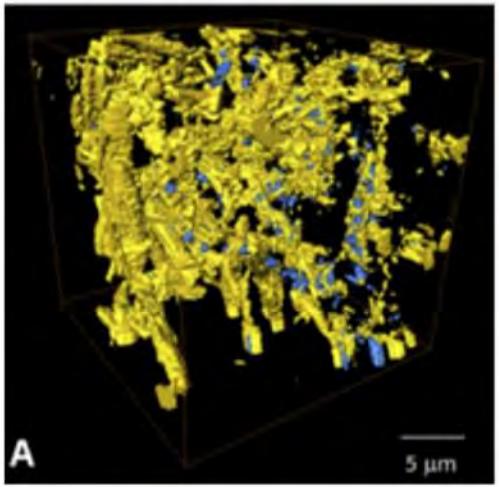
H2020-MSCA-ITN-2016/721451

Introduction

What is known on leaching of corrosion inhibitors?

Transport of active corrosion species

- Network of interconnected clusters of soluble material

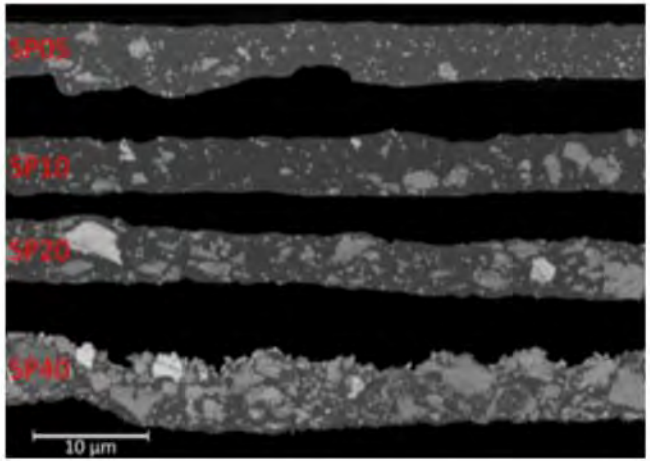


3D Electron tomography showing $SrCrO_4$ particles (yellow) and associated voids (blue) created by the dissolution of the $SrCrO_4$ particles.

A.E. Hughes et. al, *Progress in Organic Coatings*, 77, **2014**, 1946-1956

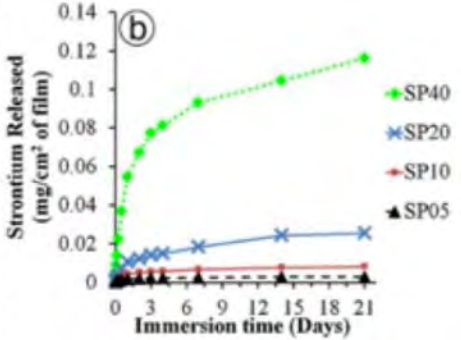
Effect of the pigment Volume Concentration (PVC)

- Increases the volume of pigment clusters resulting in higher leaching rates of active species



SEM Backscattered imaged of the cross-section of the primer with different PVC.

Emad et al. *Progress in Organic Coatings*, **102**, 71-81 (2017)

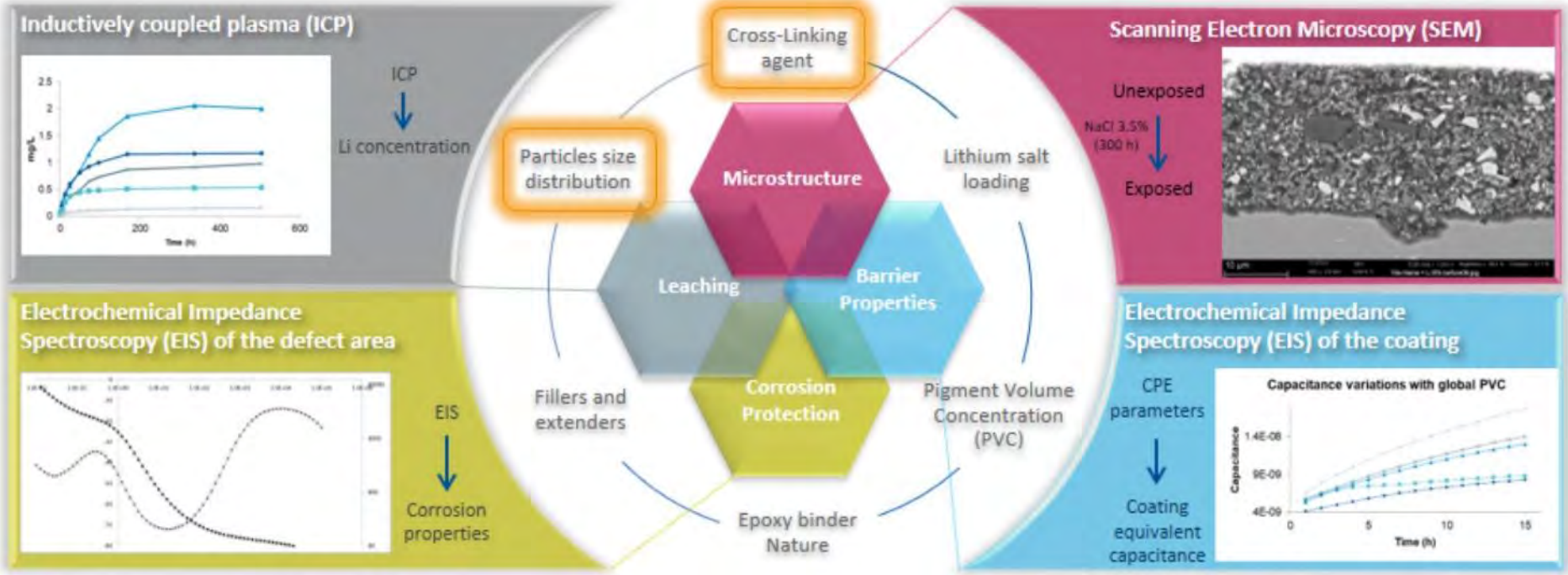


Cumulative release of Strontium per unit area of the primer

H2020-MSCA-ITN-2016/721451

Introduction

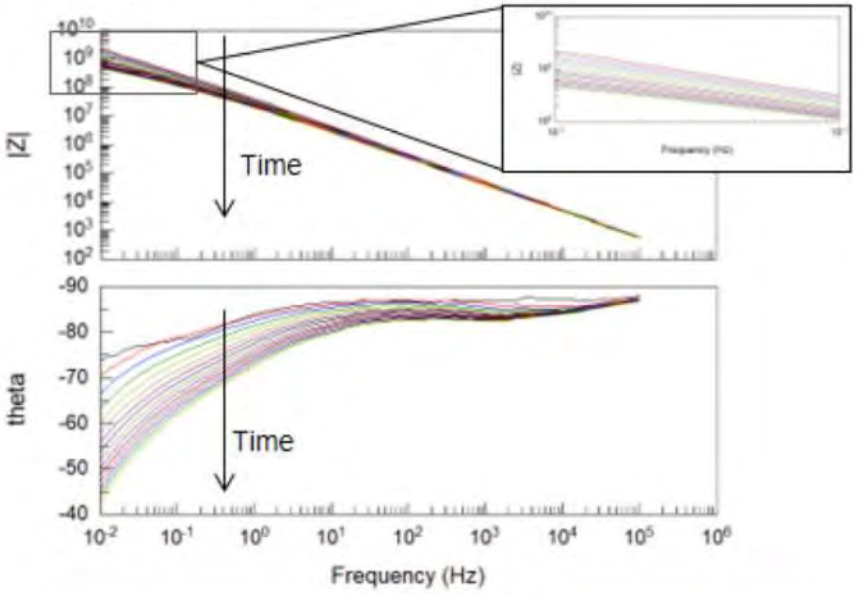
Objective and research approach

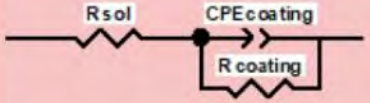


H2020-MSCA-ITN-2016/721451

Employed methodologies

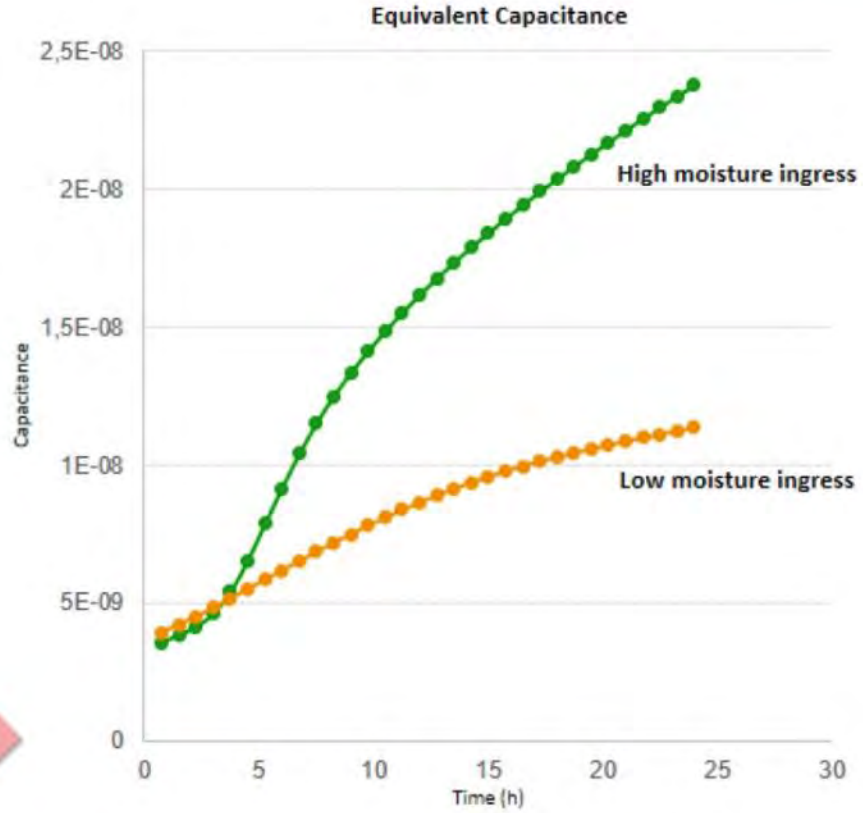
1 week moisture ingress using electrochemistry impedance
Solution: Na_2SO_4 3,5% wt





$$C = R^{\frac{(1-n)}{n}} Q^{\frac{1}{n}}$$

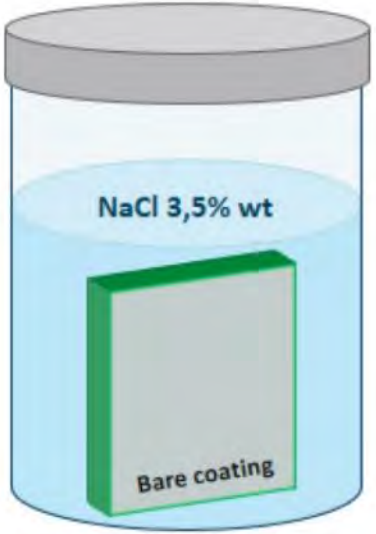
B. Hirschorn et al. *Elecgtrochimica Acta, 55 (2010), 6218-6227*



H2020-MSCA-ITN-2016/721451

Employed methodologies

1,5 weeks immersion
Solution: NaCl 3,5% wt



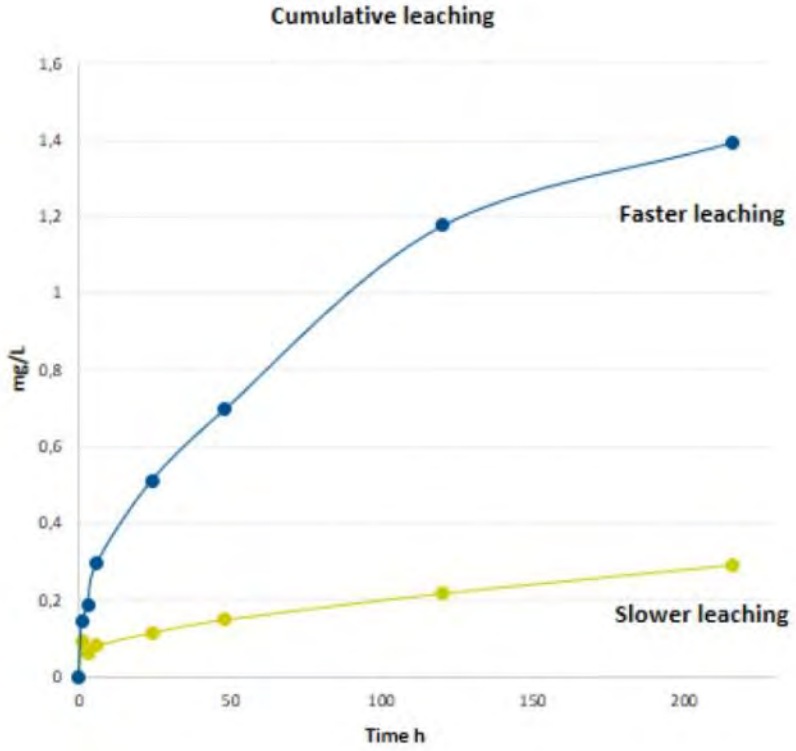
Plastic container
- Lithium tends to addere to glass

Set-up

Constant Volume: 250 ml NaCl 3,5%
Aliquots: 2 ml
Panels area: 25cm²
Duration: 1,5 weeks

ICP Measurements

Diluted to 1/4
Acidified 2% HNO_3

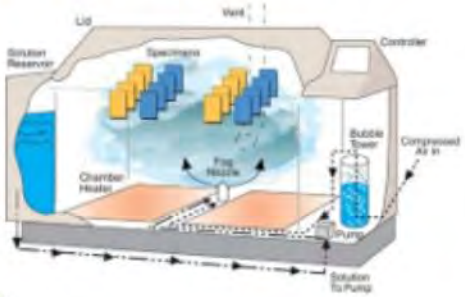


H2020-MSCA-ITN-2016/721451

Employed methodologies

1st

Scribing pannels
2,5cm x 2,5cm/1 mm deep

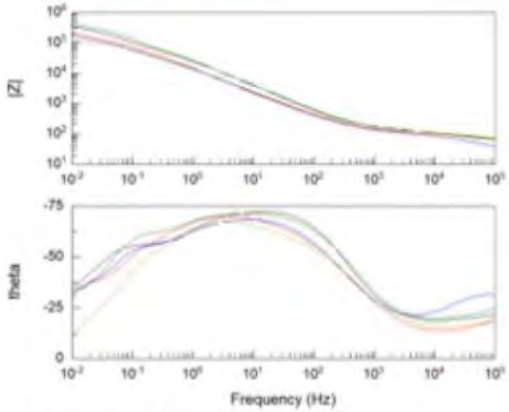


2nd

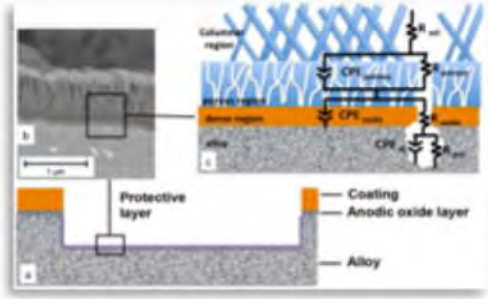
Neutral Salt Spray (NSS 168 h)
Formation of protective layer

3rd

Electrochemical impedance spectroscopy
0.05 M NaCl solution



Active corrosion protection

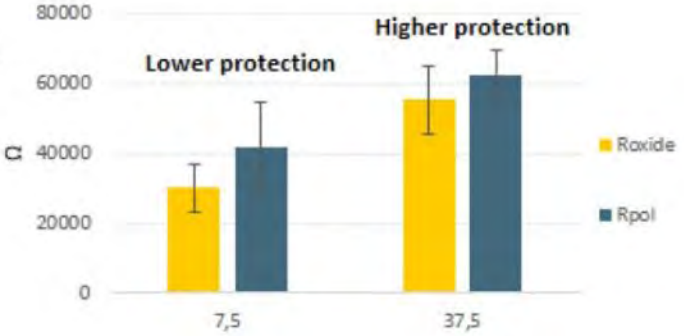


Visser et al. *Journal ofThe Electrochemical Society*, **164** (7) C396-C406 (2017)

4th

Fitting with the physical model which represents the protective layer structure

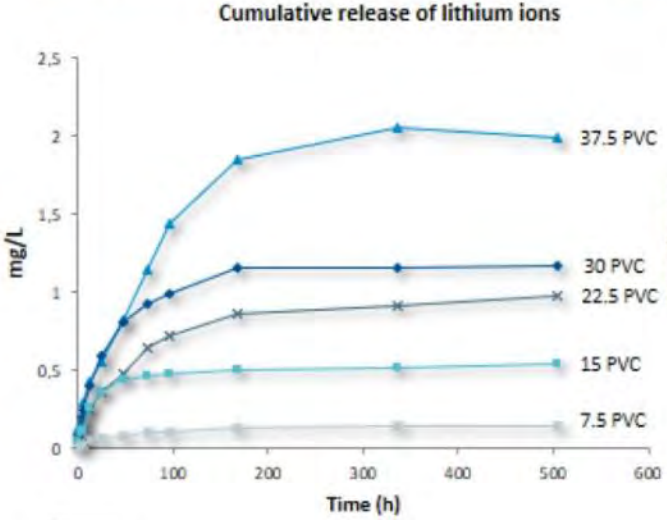
- R oxide rayer (R_{oxide})
- R polarization resistance (R_{pol})

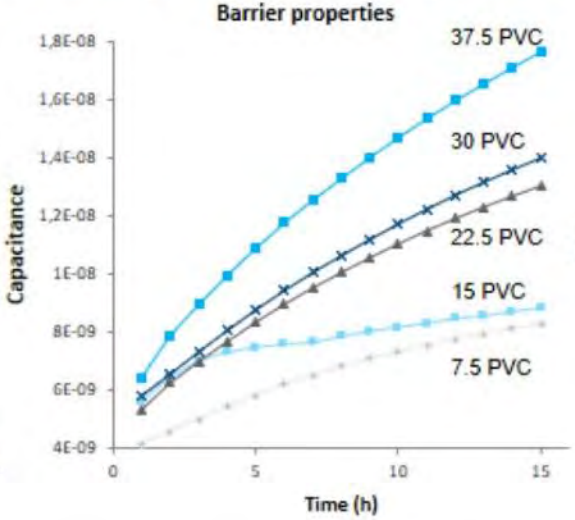


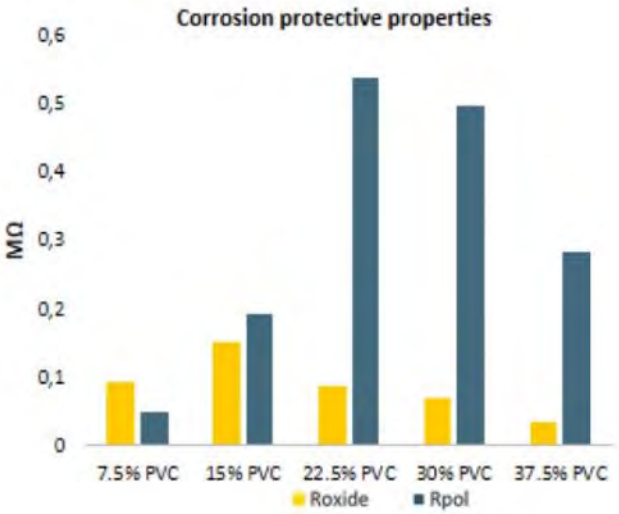
H2020-MSCA-ITN-2016/721451

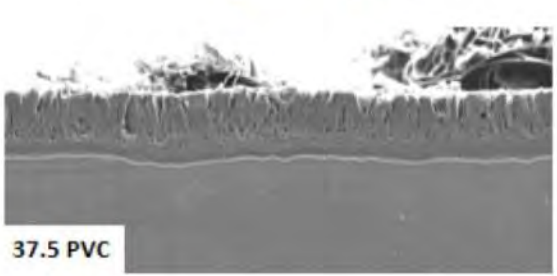
The effect of the PVC

Lithium leaching, Barrier and corrosion protection properties





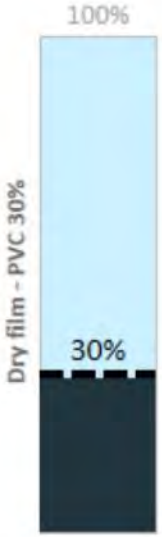




H2020-MSCA-ITN-2016/721451

The effect of the Particles Size Distribution

Lithium leaching and corrosion protection properties



Substrate
AA2024-T3 Bare TSA 0.8 mm

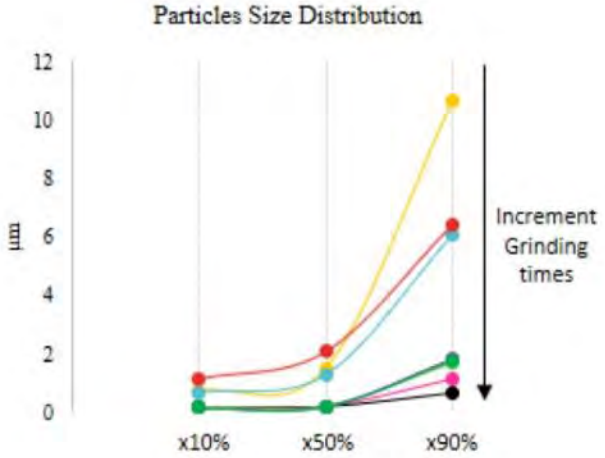
System of study
Binder: Bisphenol A base-resin – group content 5260-5420 mmol/kg; molar mass 184-190 g

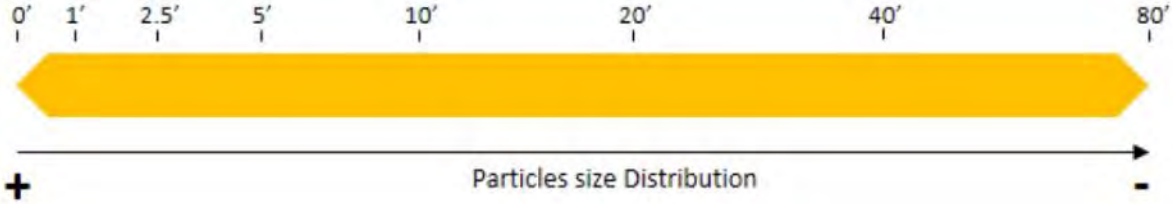
Aliphatic amine cross-linking agent: equivalent weight 135 Wt/{H}; amine value 350-380 mg KOH/g

Pigment volume concentration (PVC): 30%
Pigments (vol%): 8.3% Li_2CO_3, 7.7 MgO, 7% TiO_2, 7% $BaSO_4$

Layer thicknesses – average of 27 µm

Grinding via shaking: Grinding times

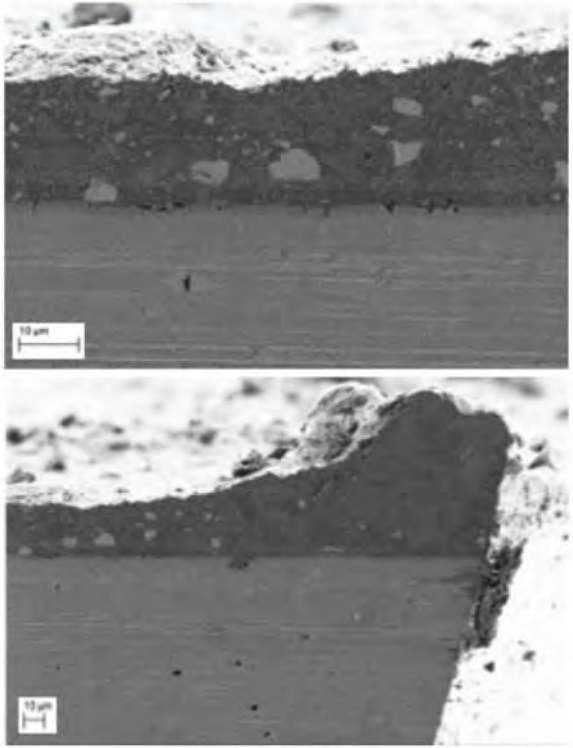




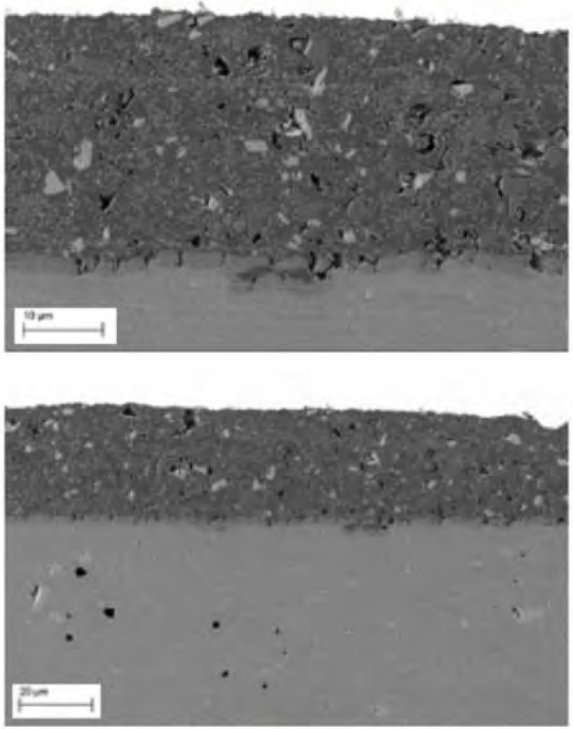
H2020-MSCA-ITN-2016/721451

The effect of the Particles Size Distribution

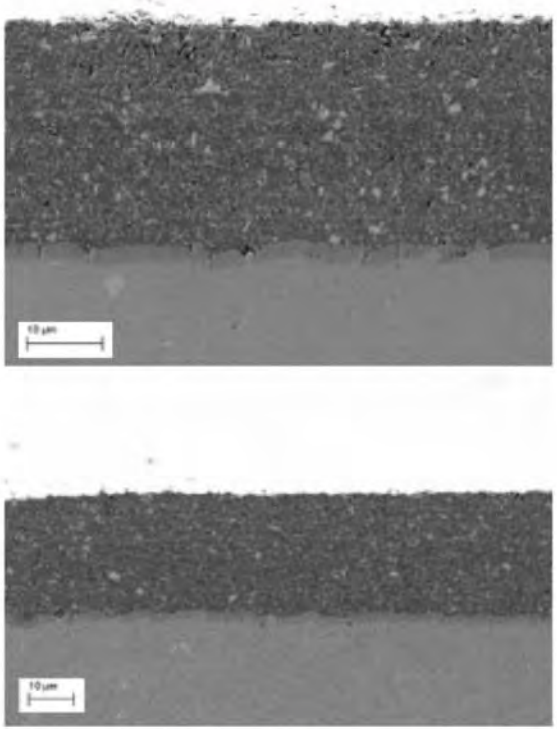
Coating microstructure



30PVC-tim-1’



30PVC-tim-10’

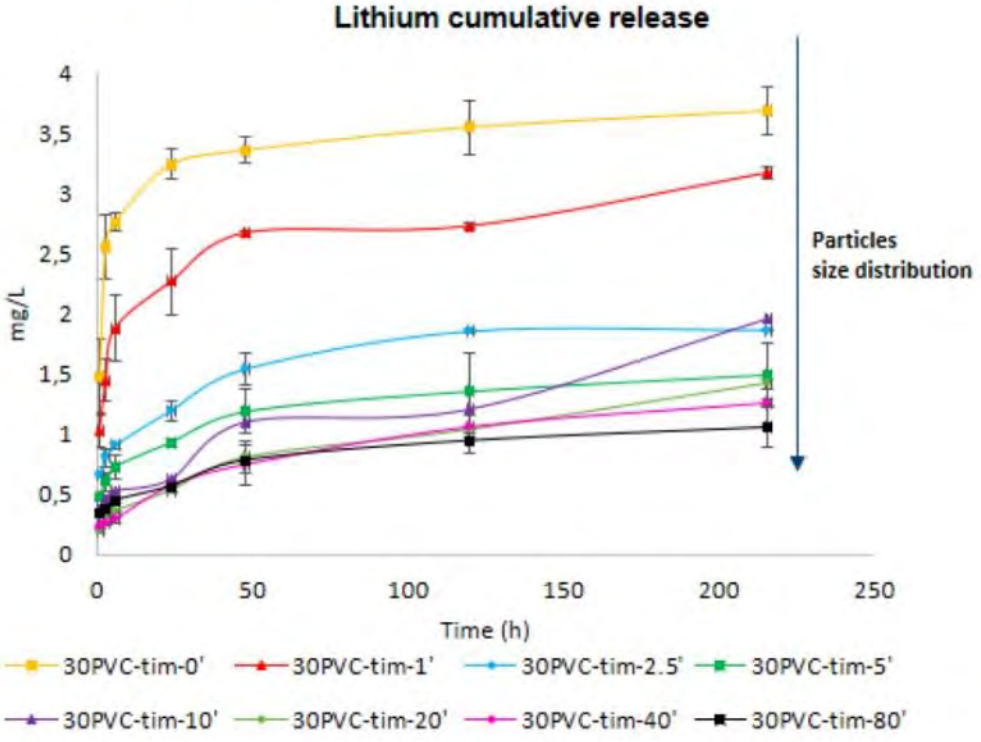


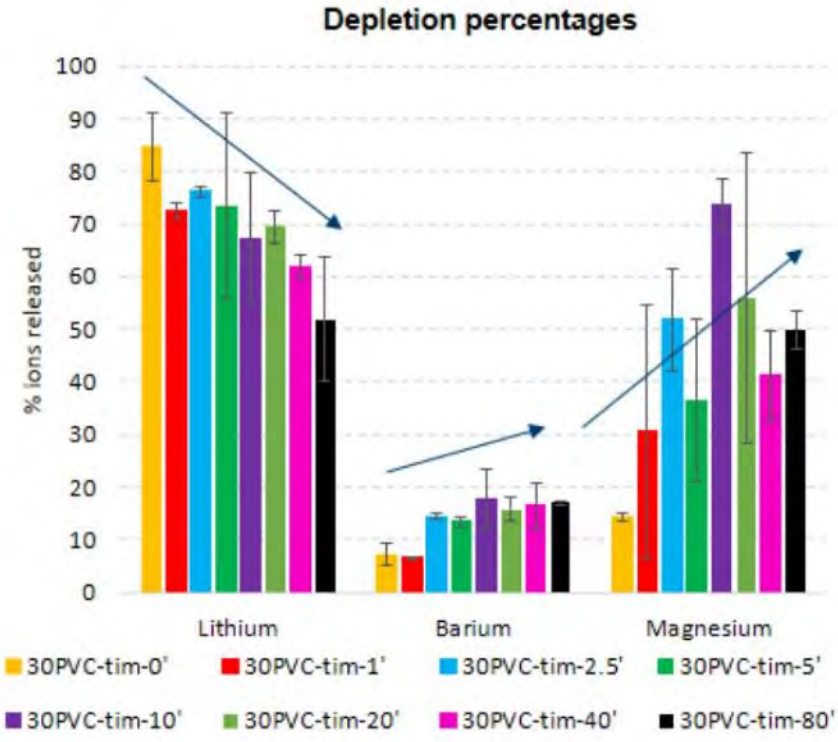
30PVC-tim-80’

H2020-MSCA-ITN-2016/721451

The effect of the Particles Size Distribution

Leaching Properties



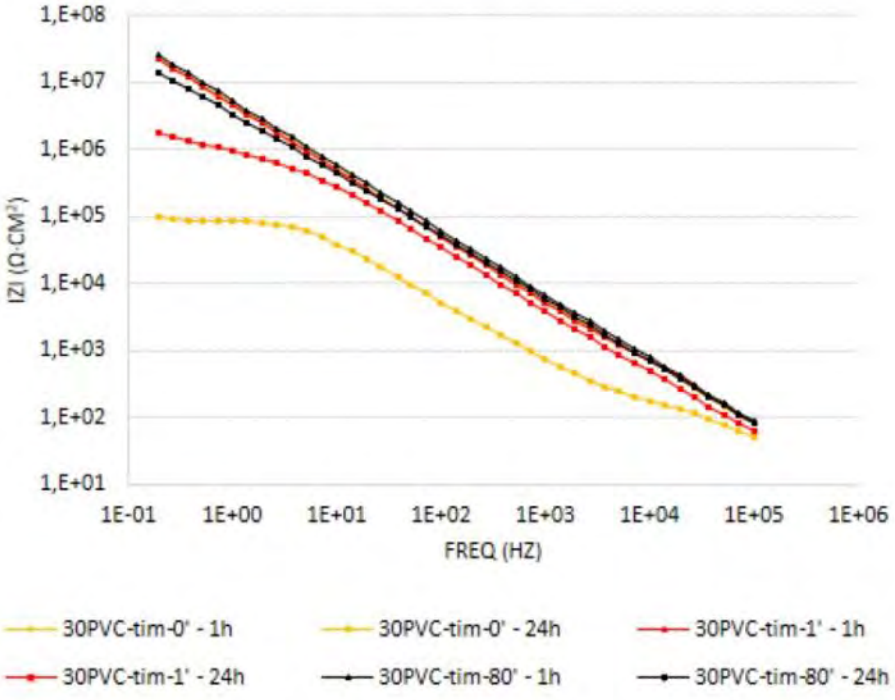


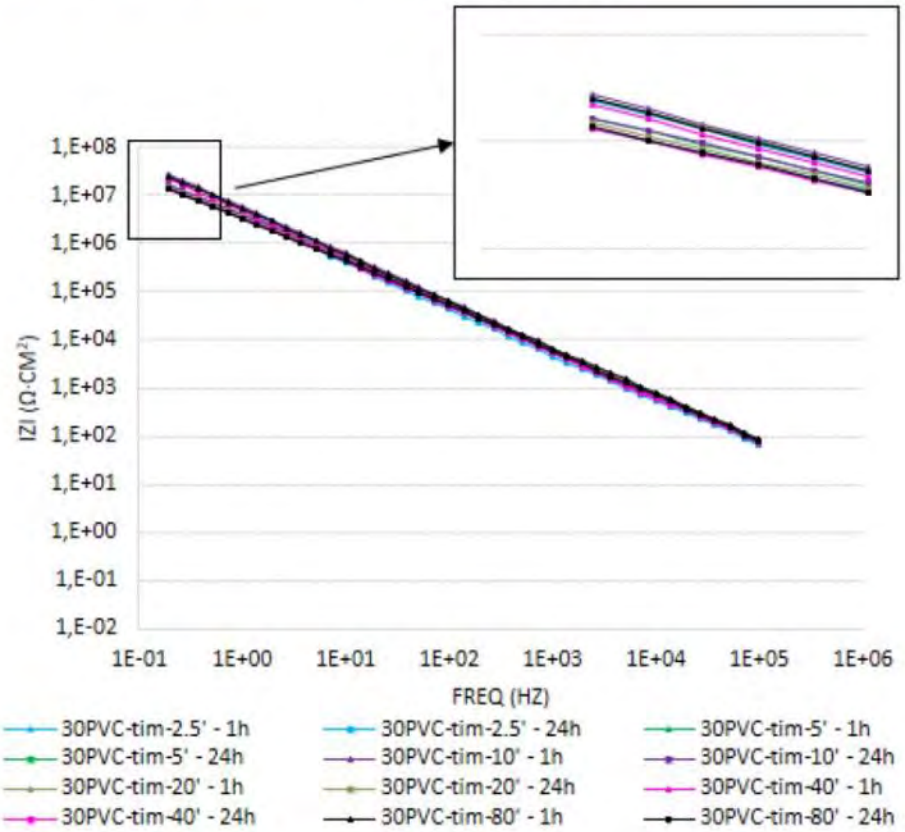
H2020-MSCA-ITN-2016/721451

The effect of the Particles Size Distribution

Barrier Properties

- **Barrier properties decrease with smaller particles size distribution values**



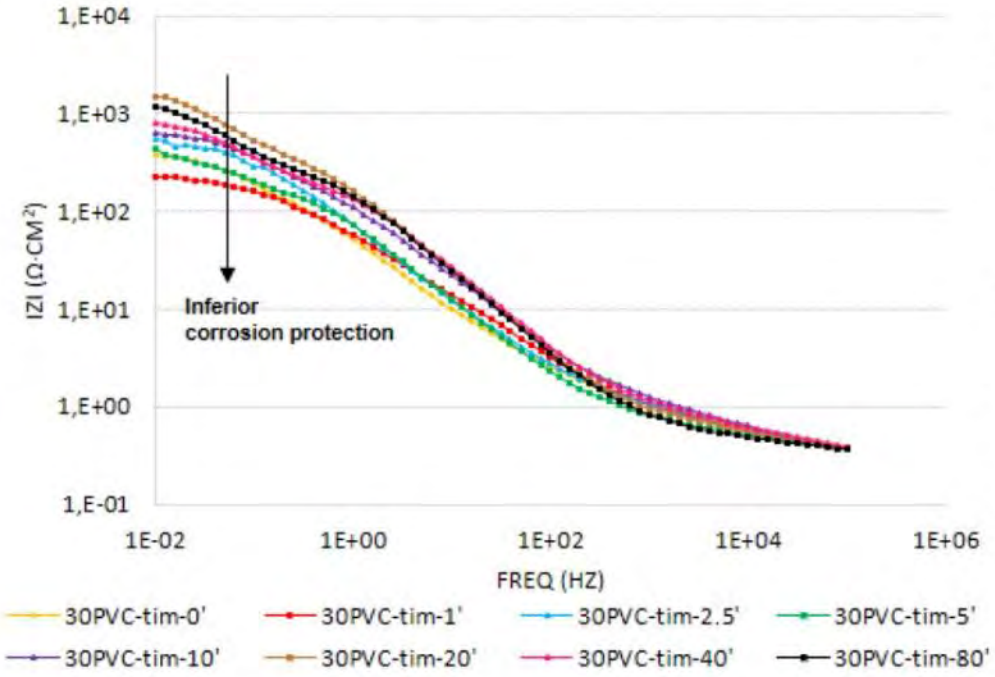


H2020-MSCA-ITN-2016/721451

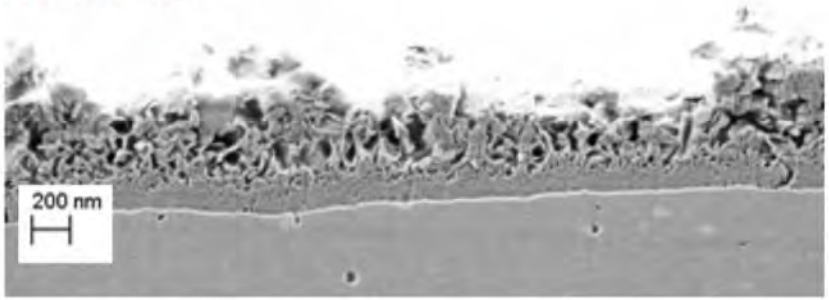
The effect of the Particles Size Distribution

Corrosion protection properties

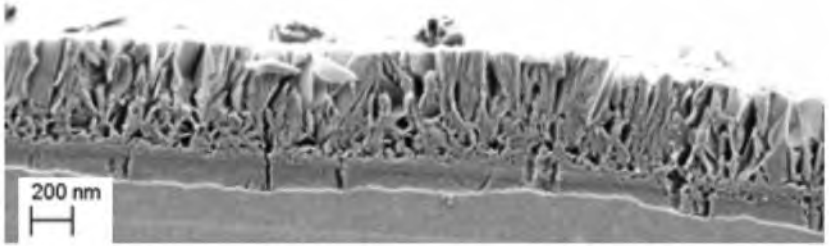
- **Slower lithium leaching provides superior corrosion protection**



30PVC-tim-1'



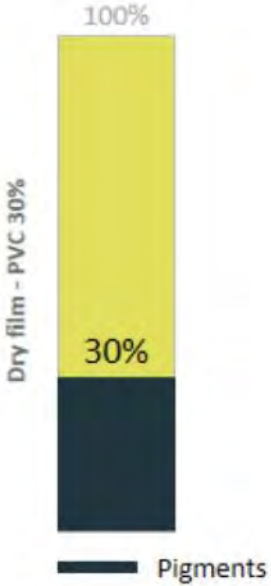
30PVC-tim-80'



H2020-MSCA-ITN-2016/721451

The effect of the cross-linking agent

Systems of study



Substrate
AA2024-T3 Bare TSA 0.8 mm

System of study
Binder: Bisphenol A base-resin – group content 5260-5420 mmol/kg; eew . 184-190 g

Curing Agents:

(A) Modified aliphatic amine: Outstanding chemical resistance; ew 88 Wt/{H}
(B) Aliphatic amine: Good chemical resistance; eq 135 Wt/{H}
(C) Aliphatic amine adduct: Good chemical resistance; ew 45 Wt/{H}
(D) Modified polyamide: Good corrosion protection; ew 114 Wt/{H}
(E) Aliphatic polyether diamine: Water soluble and high flexibility; ew 132 Wt/{H}
(F) Amidoamine: Excellent immersion resistance in aqueous media; ew 93 Wt/{H}
(G) Cycloaliphatic amine: no VOC content; ew 82 Wt/{H}

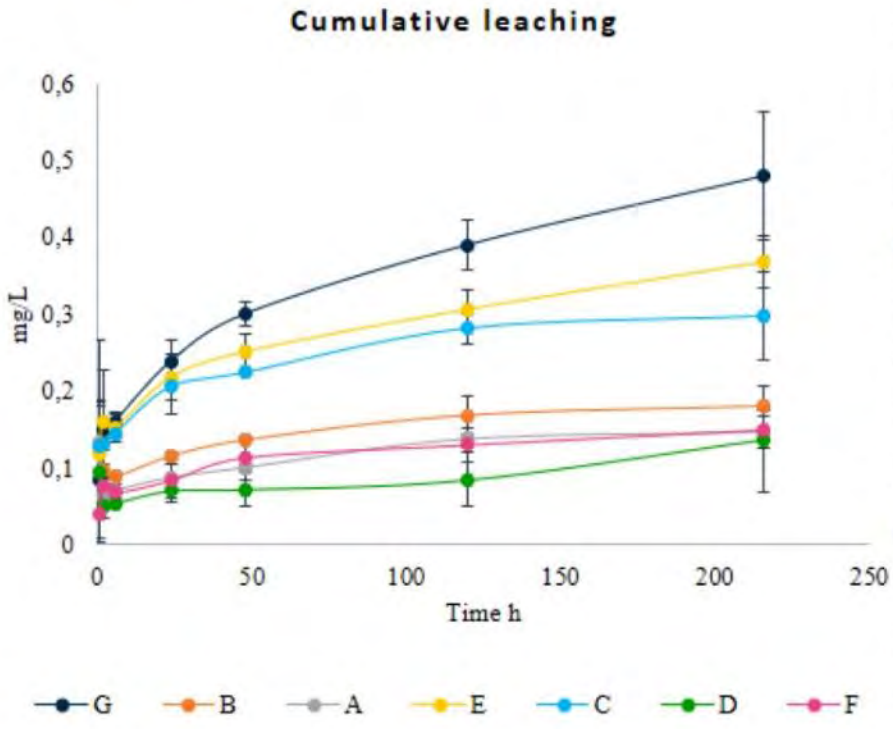
Pigment volume concentration (PVC): 30%
Pigments (vol%): 8.3% Li_2CO_3, 7.7 MgO, 7% TiO_2, 7% $BaSO_4$

Layer thicknesses – average of 27 µm
Fineness of grind – max 15 µm

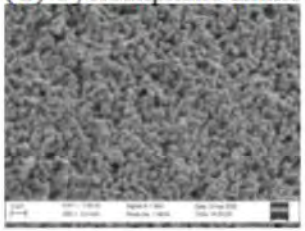
H2020-MSCA-ITN-2016/721451

The effect of the cross-linking agent

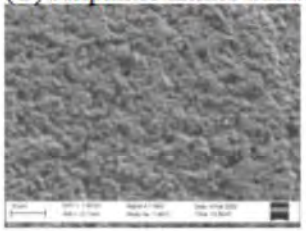
Leaching Properties



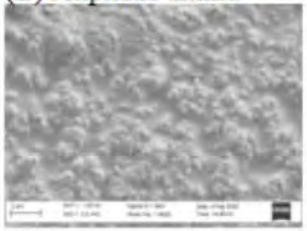
(G) Cycloaliphatic amine



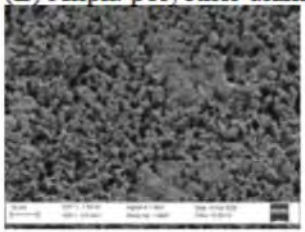
(C) Aliphatic amine adduct



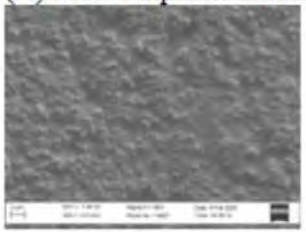
(B) Aliphatic amine



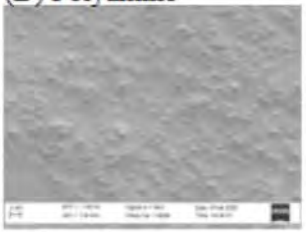
(E) Aliph. polyether diamine



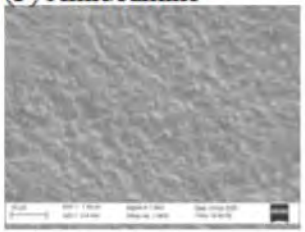
(A) Mod. Aliphatic amine



(D) Polyamine



(F) Amidoamine



- **Rougher surfaces lead to faster leaching of Li-based corrosion inhibitor**

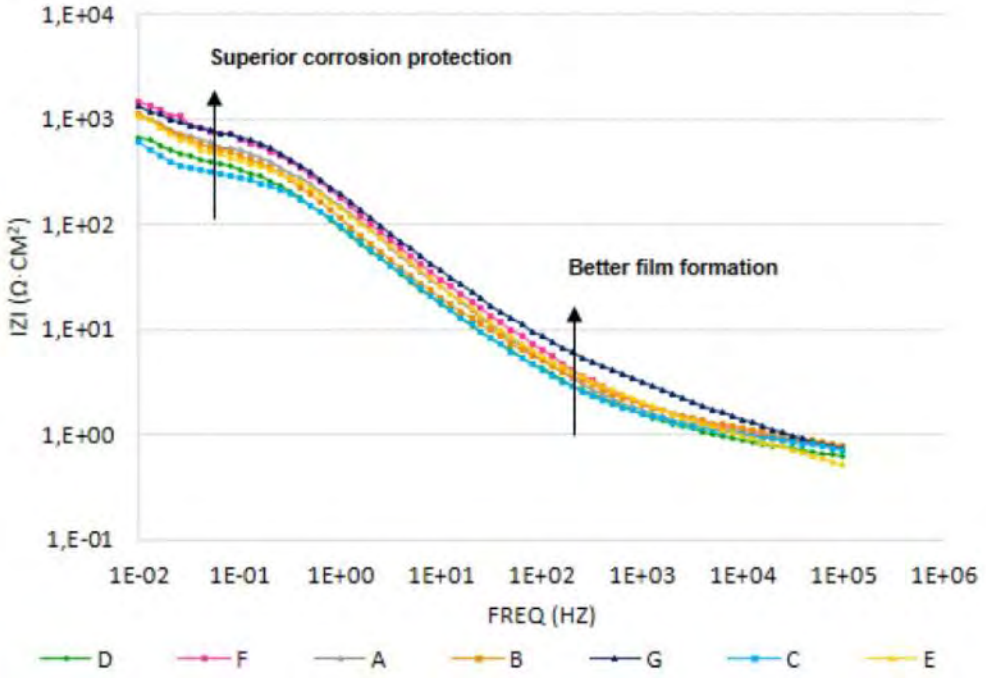
H2020-MSCA-ITN-2016/721451

The effect of the cross-linking agent

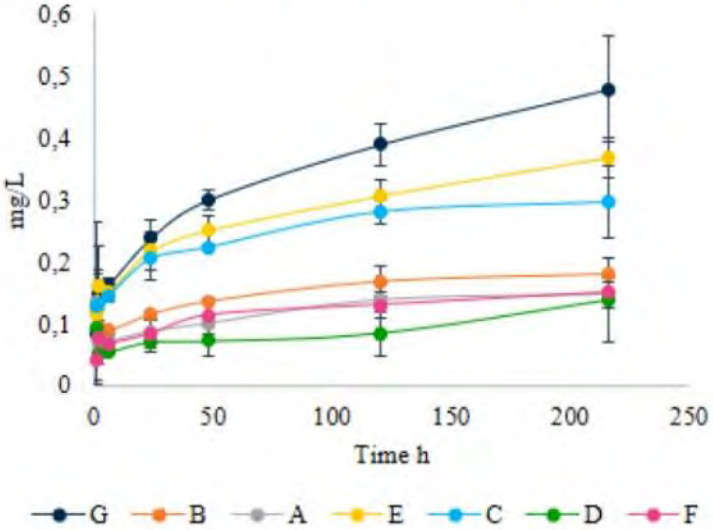
Corrosion protection properties

MANCHESTER 1824 The University of Manchester AkzoNobel

Corrosion protection



Cumulative leaching



- Amidoamine (F) system displays the highest impedance in the low (1E-02 – 1E-01 Hz), and cycloaliphatic (G) (no VOC content) system has the highest in the middle frequencies range (1E-01 – 1E-03 Hz)

H2020-MSCA-ITN-2016/721451

SUSTICOAT

Conclusions

Particles size distribution

- Variations in the particles size distribution strongly changes the connectivity between the soluble material in the coating matrix.
- Leaching of lithium inhibiting species increases with decreased particles size distribution, contrarily to these of magnesium and barium which increase.
- The change in the leaching rate modifies the corrosion protection performance of the systems.
- Lower average particles size distributions provide superior corrosion protection

Cross-linking agent

- The cross-linking agent has a small effect on the leaching of corrosion inhibitor. Cycloaliphatic amine displays the highest cumulative leaching.
- This translate in distinct corrosion protection performances. Where the best corrosion protection is provided in this case by the fastest leaching system, the amidoamine.

H2020-MSCA-ITN-2016/721451

AkzoNobel

MANCHESTER 1824
The University of Manchester

Thans for listening

Q & A