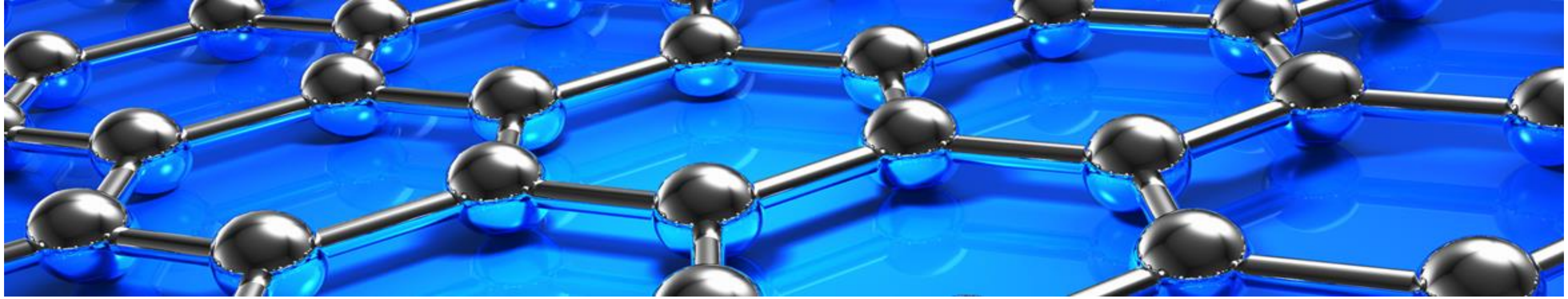

Applied Graphene Materials

Graphene in Protective Coatings

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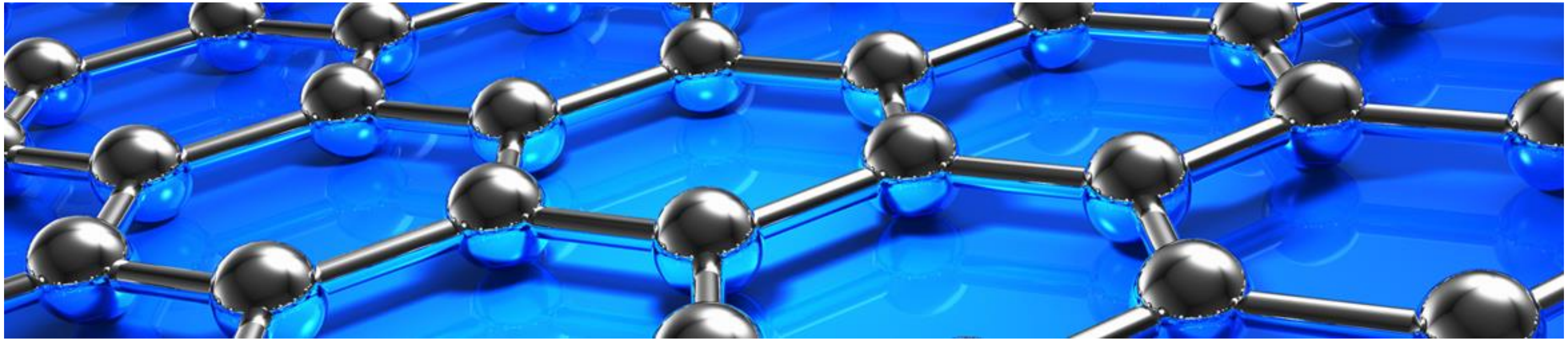
18 December 2019

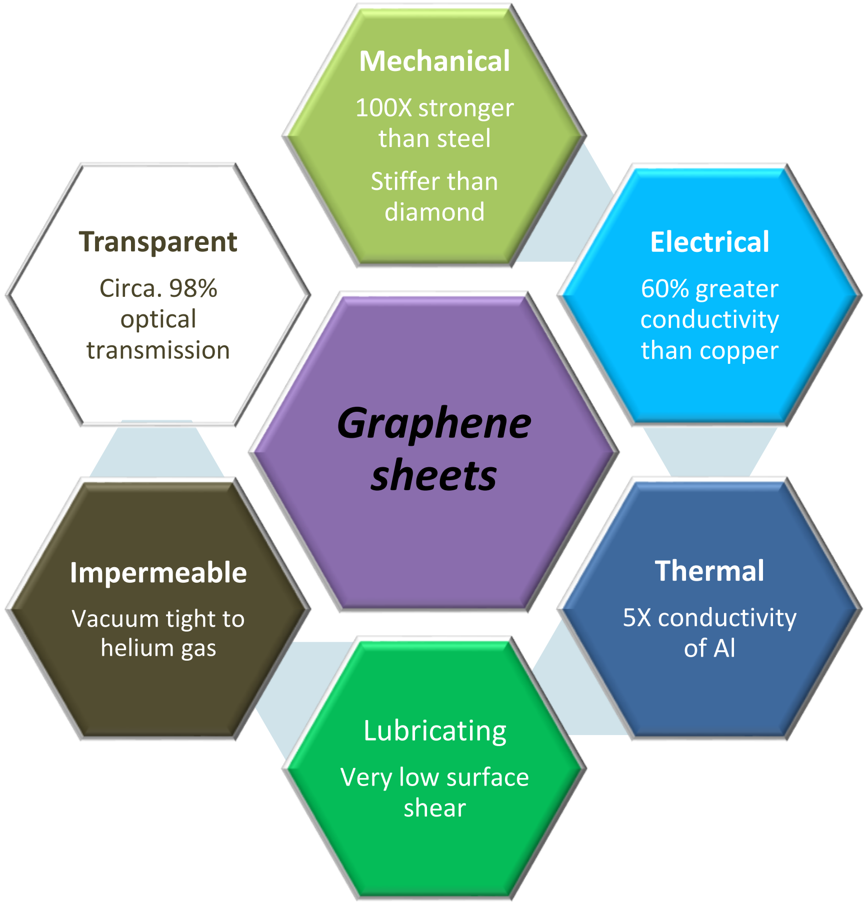


Overview

1. Introduction to Graphene
    - Graphene Nanoplatelets
    - Graphene Dispersions
2. Graphene in Industrial Epoxy Primers
    - Water Vapour Transmission Rates
    - Prohesion
    - EIS
3. Extension into Highly Corrosive Environment
4. Further work

Introduction to Graphene

Graphene – Remarkable Performance



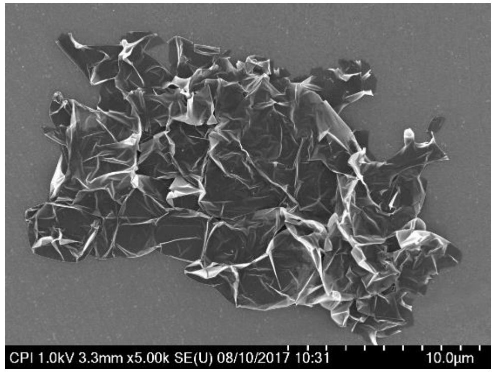
- Isolated in 2004 at University of Manchester
- Nobel prize in 2010
- Multiple forms from single layer to nanoplatelets with multiple morphologies

Key Challenge – How to unlock the potential of this exciting materials technology?

Graphene – Challenge for Coatings

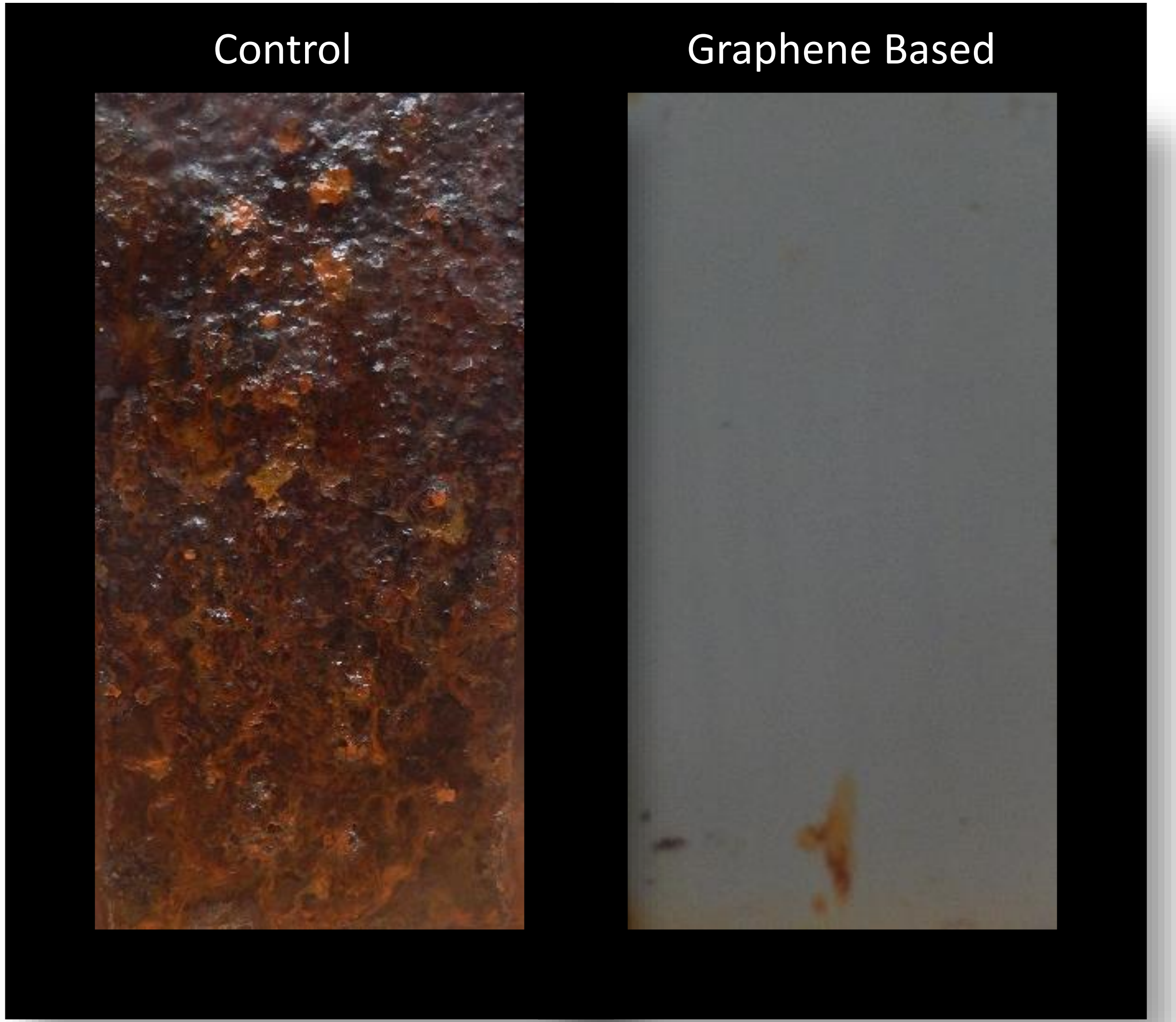
KEY FOR ALL GRAPHENE COMPANIES - How to unlock potential

- Successful Implementation into Coatings
  - Manufacture high-spec Graphenes
  - Consistent powder product



- Successful Implementation into Coatings - Dispersion chemistry - key enabler for successful use
  - Range of chemistries to suit applications
  - Environmentally friendly solutions
  - Dispersion optimisation to suit end use
  - Long shelf life additives - stability
  - Ease of shipping / Ease of Use
  - Strong Technical support

Graphene – Remarkable Performance Potential



Potential - 3000hrs test in salt spray

Graphene – Benefits in Coatings

Graphene for barrier performance & anti-corrosion

Corrosion Mitigation	Asset Life Extension	Environmental Solutions
Exceptional anti-corrosion performance	Life extension to coatings	Lower VOC and toxics
Enhanced Corrosion control	Maintenance cost reduction	Water-based technology

Use of Graphene in Coatings

A variety of mechanisms are proposed in literature by which graphene delivers anticorrosion performance

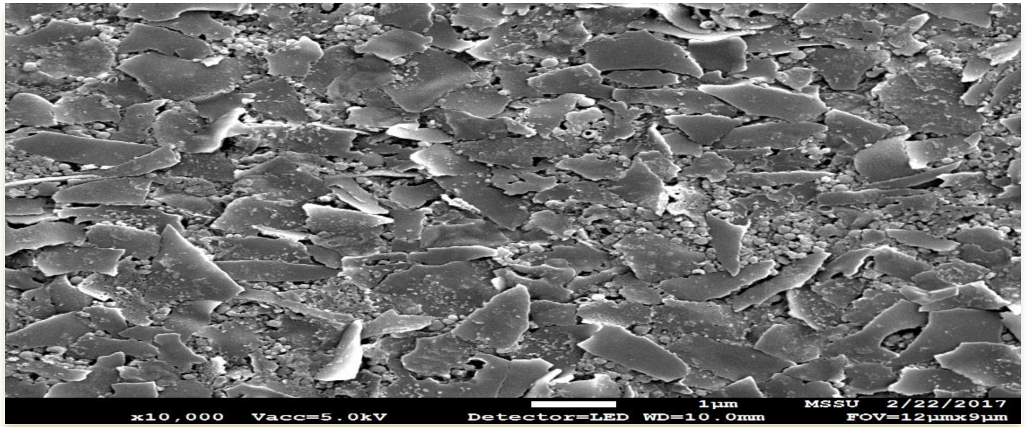
- a physicochemical process which restricts uptake of water/oxygen and salts.
- electrochemical activity.

Platelike materials such as glass flake and micas have historically been used as barrier pigments that provide a *tortuous path* in anticorrosion primers. Graphene offers a step change two-dimensional structure which delivers:

- high aspect ratio
- large surface area
- Low density

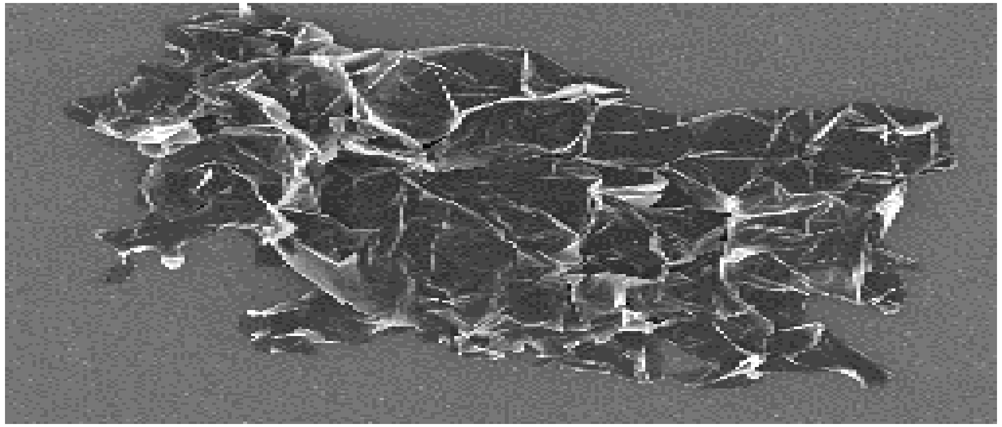
Although there have been mixed reviews in literature that suggest galvanic corrosion may be an issue with the use of graphene in anticorrosive primers, this has not been observed in our testing. This may be the result of the very low levels of graphene used, which are below the percolation threshold.

AGM Graphene Nanoplatelets – Product Properties



Grade 10

- Reduced Graphene Oxide – approximately 15% Oxygen
- Synergistic performance when combined with other active inhibitors
- Moderate density and surface area allows high loading levels. Standard dispersions loaded at 10% GNP
- Recommended active Graphene addition between 0.25% → 1.0% of total formulation



Grade 35

- Few Layer Graphene – approximately 5% oxygen
- Very low density and high surface area, enabling enhanced corrosion resistance at very low loadings.
- Standard dispersion loaded at 0.5% in solvents systems and 1% GNP for the resin based products
- Recommended active Graphene addition between 0.025% → 0.1% of total paint formulation

Graphene Dispersions

AGM supplies its Graphenes in stable dispersions that are:-

- ✓ Ready to use and easy to incorporate
- ✓ Available in a number of safe to handle formats
- ✓ Optimized to impart specific performance enhancements

Genable® 1000 series

- *Designed to enhance barrier and anti-corrosion performance, especially in synergy with existing active ingredients*

Genable® 1200 series

- *Cost effective additives to enhance barrier / anti-corrosion performance at very low active loading*

Genable® 3000 series

- *Active, non-metallic, anti-corrosion additives with industry leading performance*

Standard dispersions available in:-

- *Epoxy*
- *MEK*
- *Butyl Acetate*
- *Ethyl Acetate*
- *Xylene*
- *Water*

Custom dispersions also available

Objectives of this Work

Demonstrate improved anticorrosive performance

1. By using commercially available and ready to use Graphene dispersions, optimised for use in existing coatings systems.
2. And identify significant uplifts in life expectancy and performance through use of Graphene nano-platelets

Graphene in Industrial Epoxy Primers

Test Program

Demonstrating anticorrosive performance and extended lifetime in a typical Industrial Epoxy Primer:

Water Vapor transmission (WVTR) Testing

Prohesion Testing

ASTMG85 annex 5

Duplicate panels were prepared for assessment at intervals of 500, 1000, 2000, 3000, and 5000 hours

Electrochemical studies

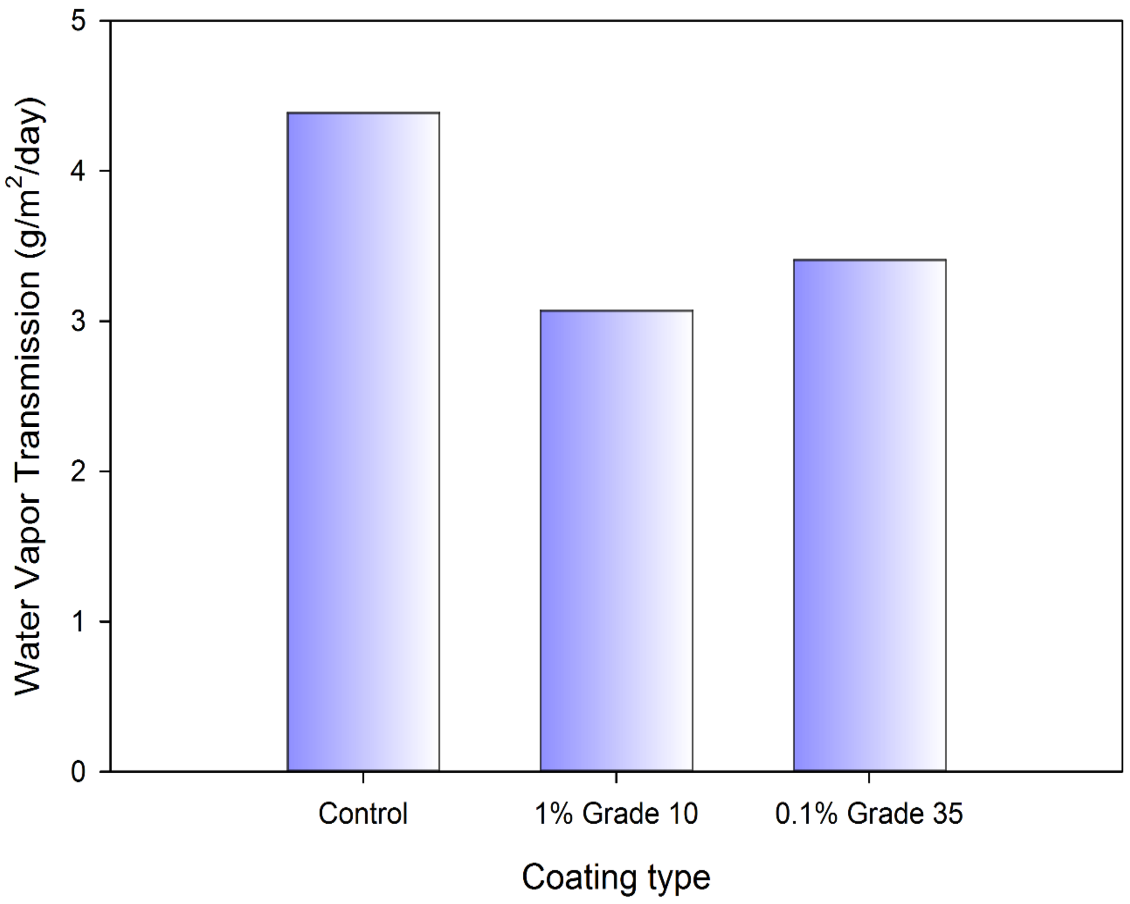
Novel Test Method looking at both scribed and unscribed substrates

AC Impedance Spectroscopy (AC EIS)

Panel Preparation

- Mild steel panels (CR4) of dimensions 150 x 100 x 2mm, grit blasted to SA2.5
- Coatings were applied using a conventional spray gun equipped with a 1.2mm tip
- Coating thickness - 100µm DFT
- All panels were allowed to cure for a period of 7 days at 23°C (+/-2°C).

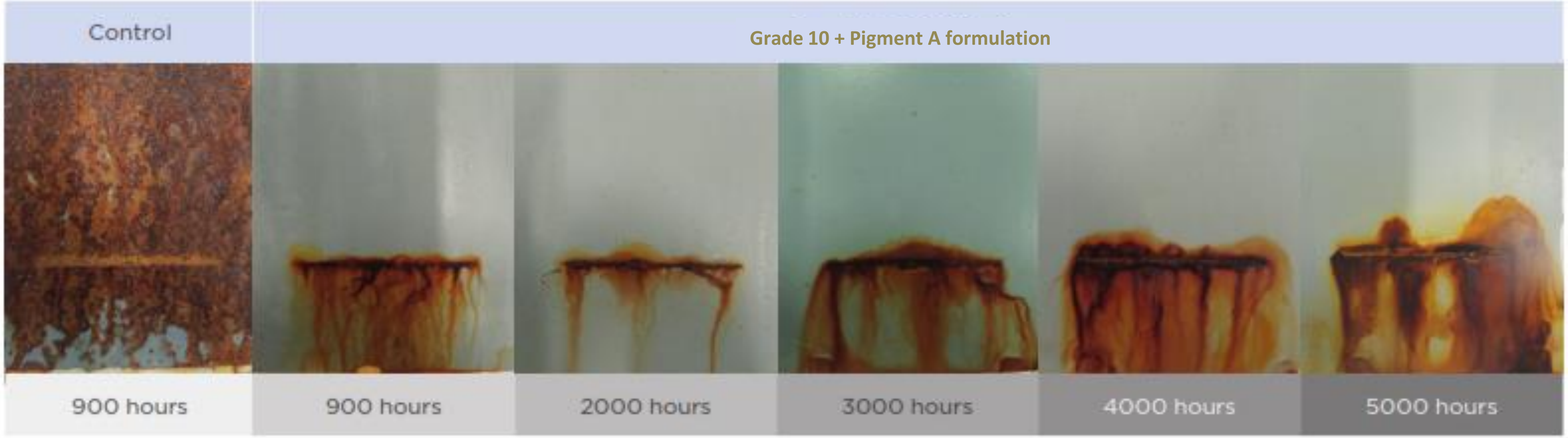
Water Vapor Transmission (WVTR)



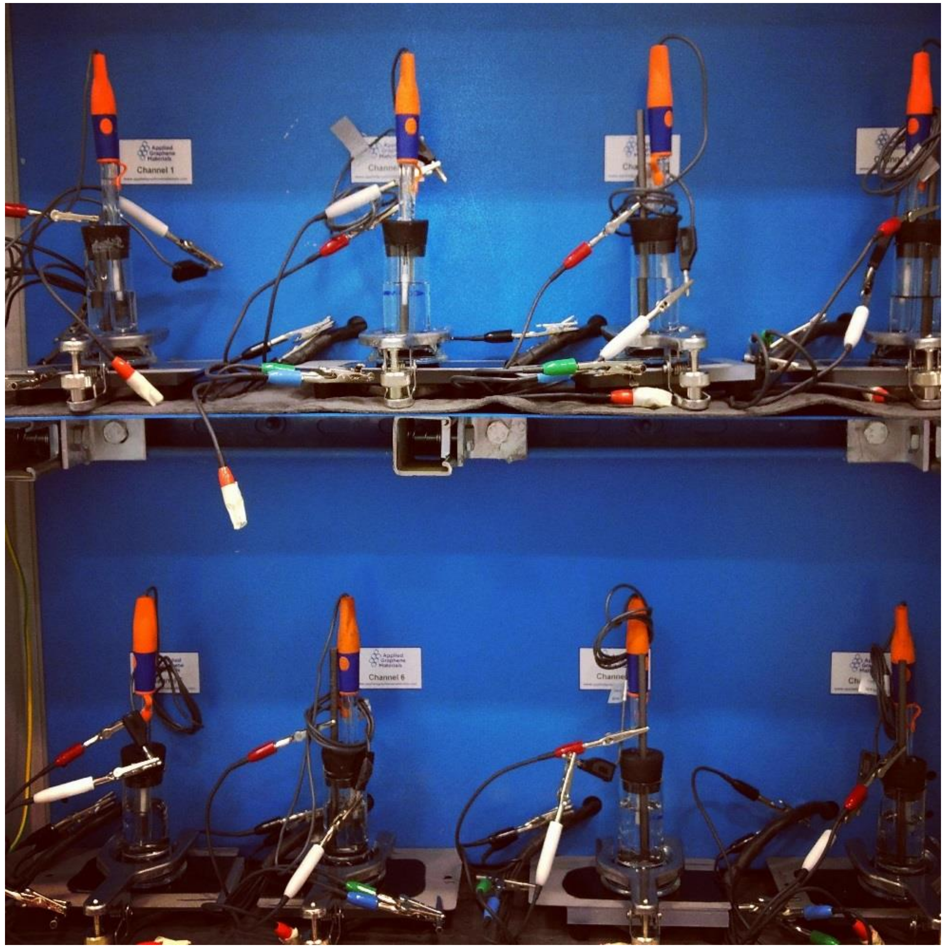
- ASTM D 1653-03 using Test Method B (wet cup method)
- The WVTR of the Control primer with Grade 10 at 1 wt.% loading was found to be the lowest with a 30% reduction in WVTR
- Grade 35 at 0.1 wt.% loading gave a 22% reduction in in WVTR

Prohesion Test Sample Images

- Prohesion Testing was carried out using ASTM G85 Annex 5 Cyclic Salt Fog test. This method allows for stronger correlation with natural exposure, as opposed to ASTM B117 (Continuous Salt Spray).
- The zinc phosphate control failed after 900 hours while the use of graphene (Grade 10) with a metal free active inhibitor extended performance up to 5000 hours.
- This early work concluded that graphene could be used to significantly improve anticorrosion performance when used in combination with actives or on its own.

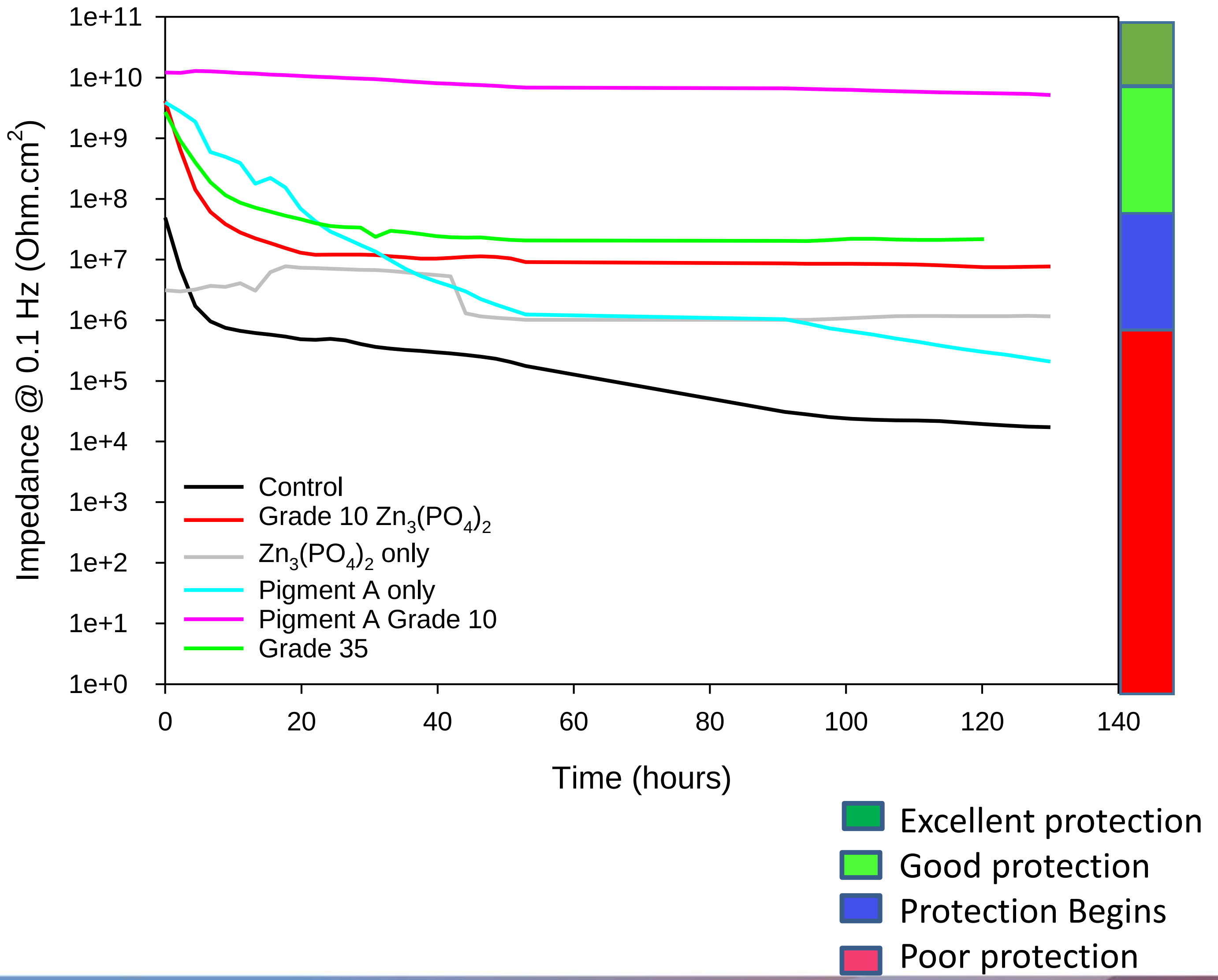


Electrochemical Testing



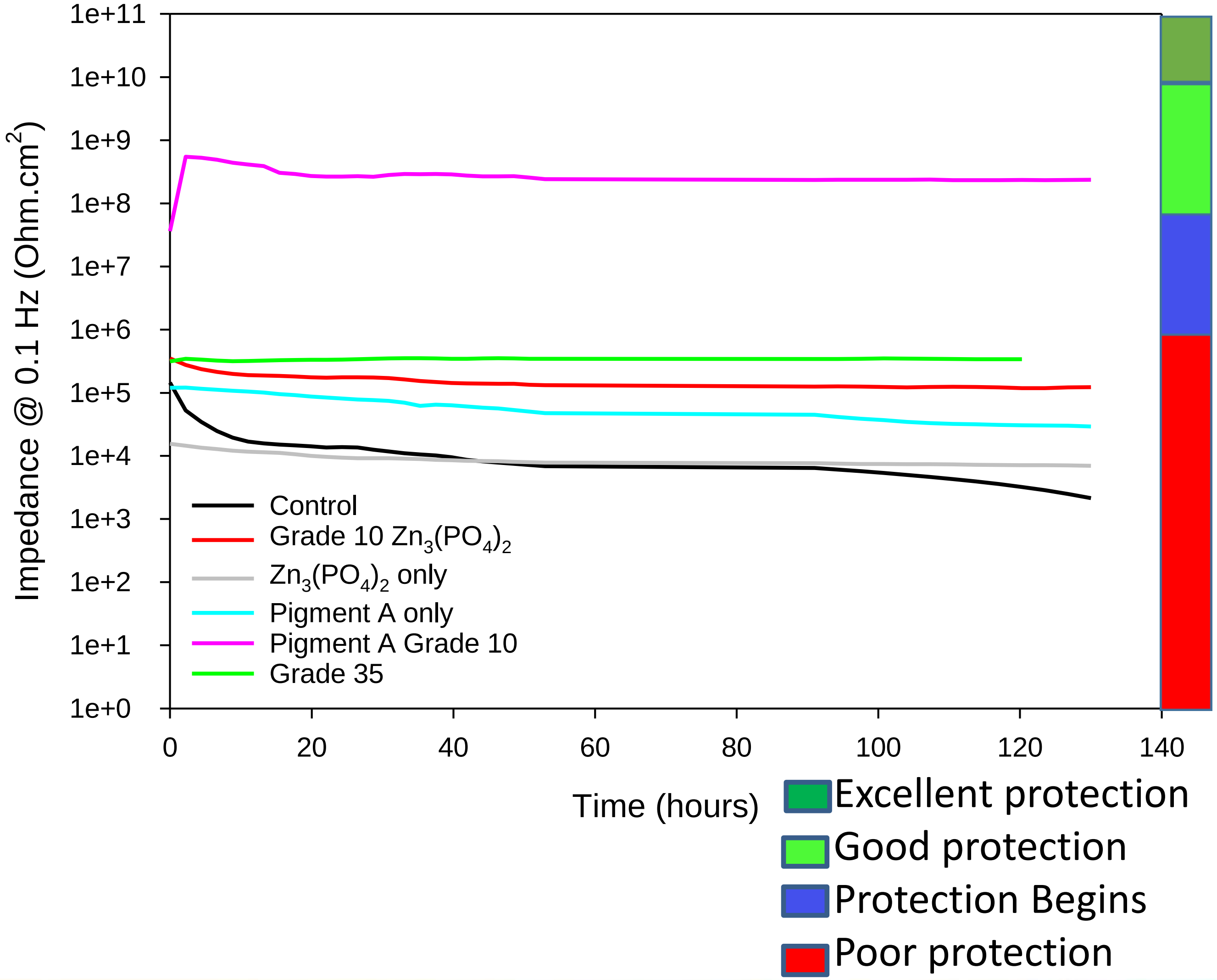
- Measurements recorded using a Gamry 1000E potentiostat in conjunction with a Gamry ECM8 multiplexer
- The test area of the working electrode was 14.6 cm^2 and run using a 3.5 wt% NaCl electrolyte
- An AC perturbation of 10 mV was applied across the samples, with a zero volt DC bias, over a frequency range of 1 MHz to 0.05 Hz
- Continuous measurements taken over a 150 hour period.

Impedance Testing (EIS) – Unscribed Coatings



- Graphene modified coatings showed higher impedance values than straight $Zn_3(PO_4)_2$ and Pigment A samples
- Inclusion of Grade 10 with $Zn_3(PO_4)_2$ gave a notably higher impedance than $Zn_3(PO_4)_2$ on its own
- Excellent (10^{10} Ohm.cm^2) impedance observed with Grade 10 with Pigment A coating over duration of test.
- Higher surface area Grade 35 alone showed significant improvement over the control.

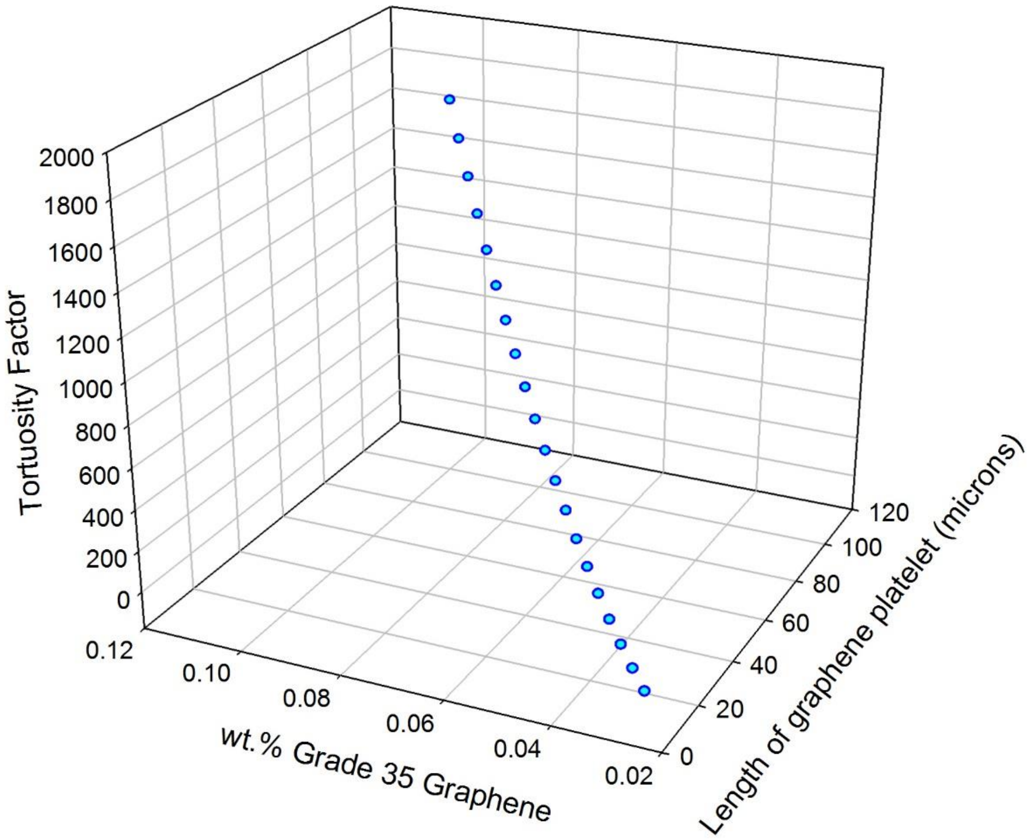
Impedance Testing (EIS) – Scribed Coatings



- Lower impedance relative to the unscribed samples as expected due to scribe presence
- Performance ranking (impedance ordering) the same as seen for the unscribed samples
- Uplift in barrier properties of coatings incorporating GNPs
- Combination of zinc phosphate with Grade 10 improved performance
- Addition of high surface area graphene (Grade 35) shows significant uplift over the control
- Grade 10/Pigment A hybrid continues to show significant performance increase in contrast to $Zn_3(PO_4)_2$ hybrids

Proposed Mechanism

- The primary mechanism of the GNP suggested is *physicochemical*, extending the diffusional pathway (tortuous path).
- Assuming that film formation (extent of cure) and PVC (pigment volume concentration) are unchanged
- The net effect is an efficient physicochemical barrier effect to water/salts :-
    - reduced rate of diffusion through the coating
    - preservation of the active pigment over the coating life
- Such a mechanism would be a function of
    - physicochemical impact of the graphene
    - graphene morphology
    - solubility and passivation rate of the active pigments



Exploitation

- Based upon good anticorrosion performance, a range of products launched with industry partners.
- Primers for anticorrosion performance :-
  - Automotive
  - Aerosols
  - Construction

Extension of Graphene Use into High Corrosivity Environments

ISO 12944 C4/C5 Systems

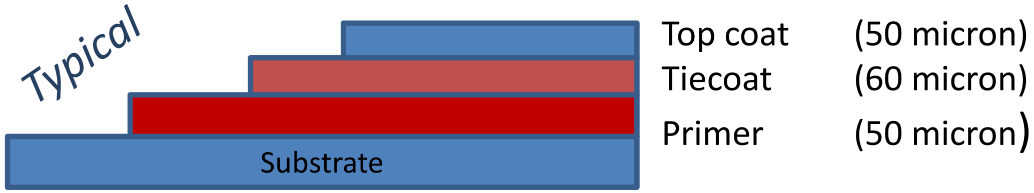
ISO 12944 distinguishes 6 basic atmospheric corrosivity categories:

C1 very low
C2 low
C3 medium
C4 high
C5 very high
CX extreme

Systems:

1. Zinc Rich Primer
2. Tiecoat – tested with and without graphene
3. Top coat

Use of Graphene Tiecoat offers the lowest risk for Graphene incorporation. This preserves the industry requirements for the zinc rich primer.



Test Panel Preparation

Steel panels of dimensions 150 x 100 x 2mm, grit blasted to SA2.5

Coatings were applied using a conventional spray gun.

Multicoat systems at 150 -160µm DFT

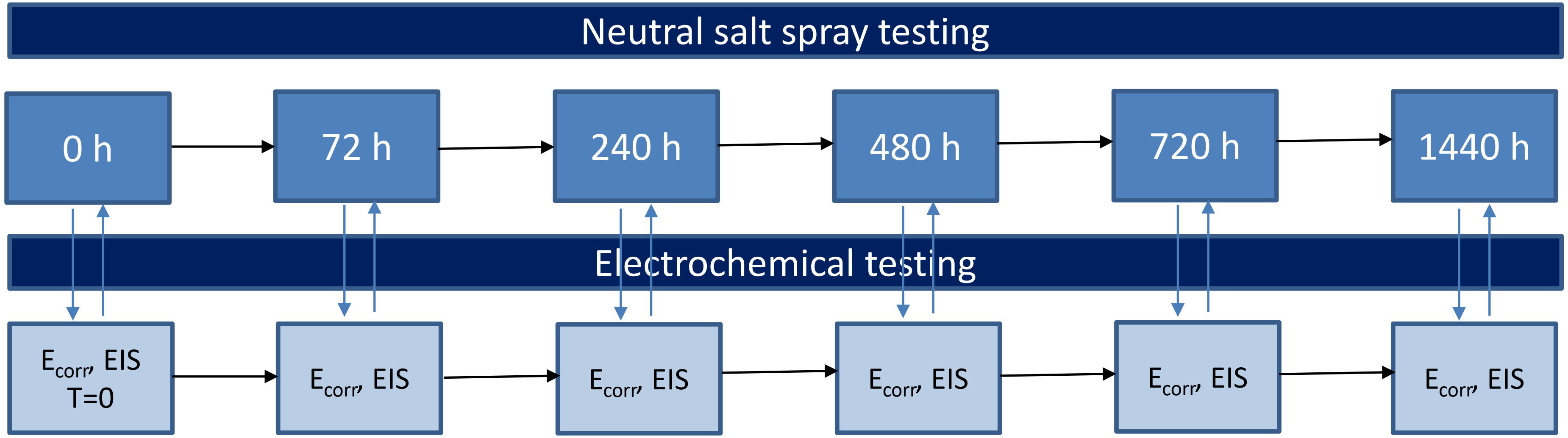
For multicoat samples the overcoating interval used was 3 hours

All panels were allowed to cure for a period of 7 days at 23°C (+/-2°C).

Tiecoat Formulations

Component	Control	Grade 10: Reduced Graphene Oxide Dispersion	Grade 35: Graphene Dispersion	Grade 10 + Pigment A: Hybrid Dispersion
Epoxy (EEW 190 g/eq)	15.119	15.119	15.119	15.119
Amino Resin	0.244	0.244	0.244	0.244
Dispersant	0.402	0.402	0.402	0.402
Xylene	15.376	15.376	15.376	15.376
Bentonite thixotrope	0.366	0.366	0.366	0.366
Butanol	1.986	1.986	1.986	1.986
Titanium dioxide	10.966	10.966	10.966	10.966
Blanc Fixe	43.619	43.619	43.619	43.619
Epoxy (EEW 190 g/eq)	**10**	**0**	**0**	**0**
GNP dispersion	**0**	**10**	**10**	**10**
Polyamine hardener	1.922	1.922	1.922	1.922
Total	100	100	100	100
GNP loading %	0	***1***	***0.1***	***0.5***

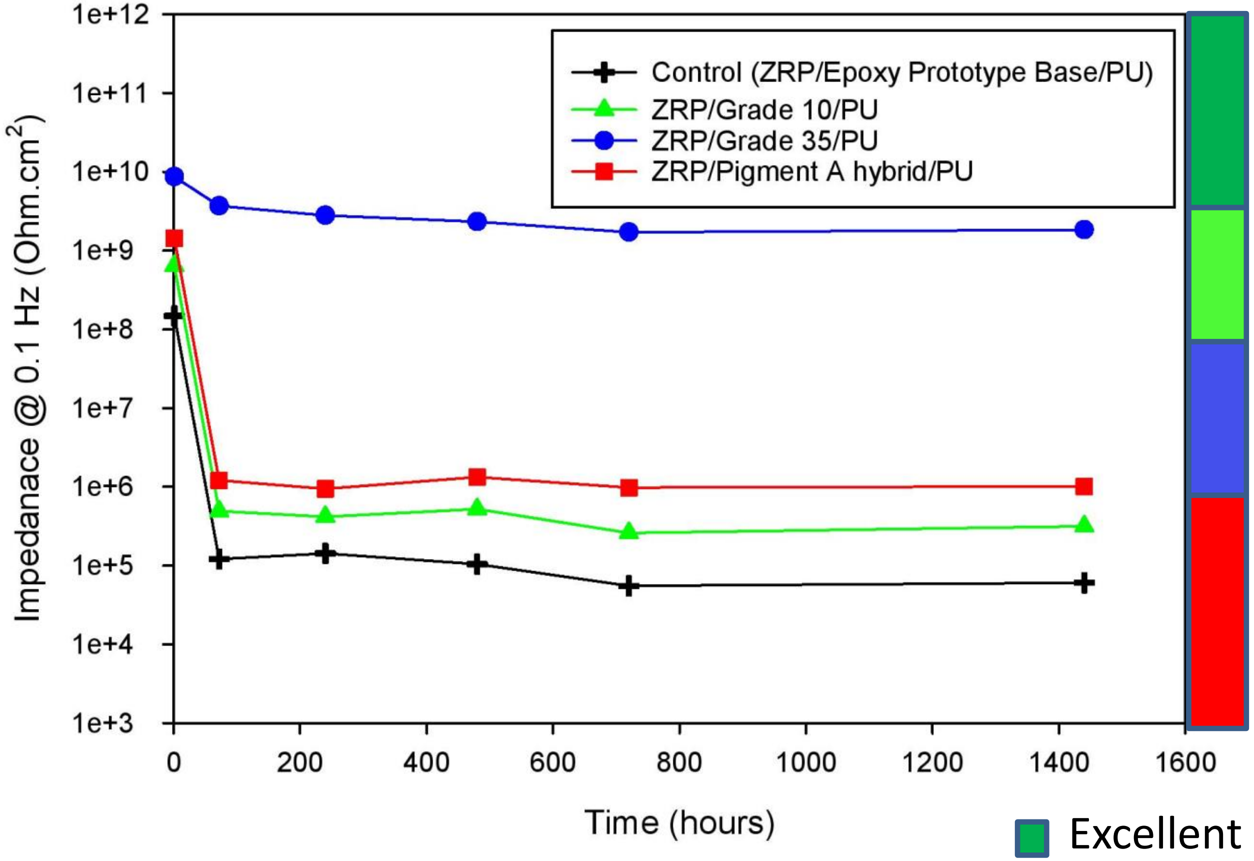
Combined EIS Testing



Dual testing approach

- Combined tests are complimentary to each other since EIS can determine relatively small changes within the coating e.g. with respect to water uptake prior to any visible coating changes noted from the examination of the test panels
- The test conditions of NSS are more realistic and accelerative compared to simply submerging the sample in NaCl solution, under ambient conditions, as is usually done during prolonged EIS studies within the paint test cell
- Where possible, test data from EIS and salt spray test results may also be used to corroborate coating performance

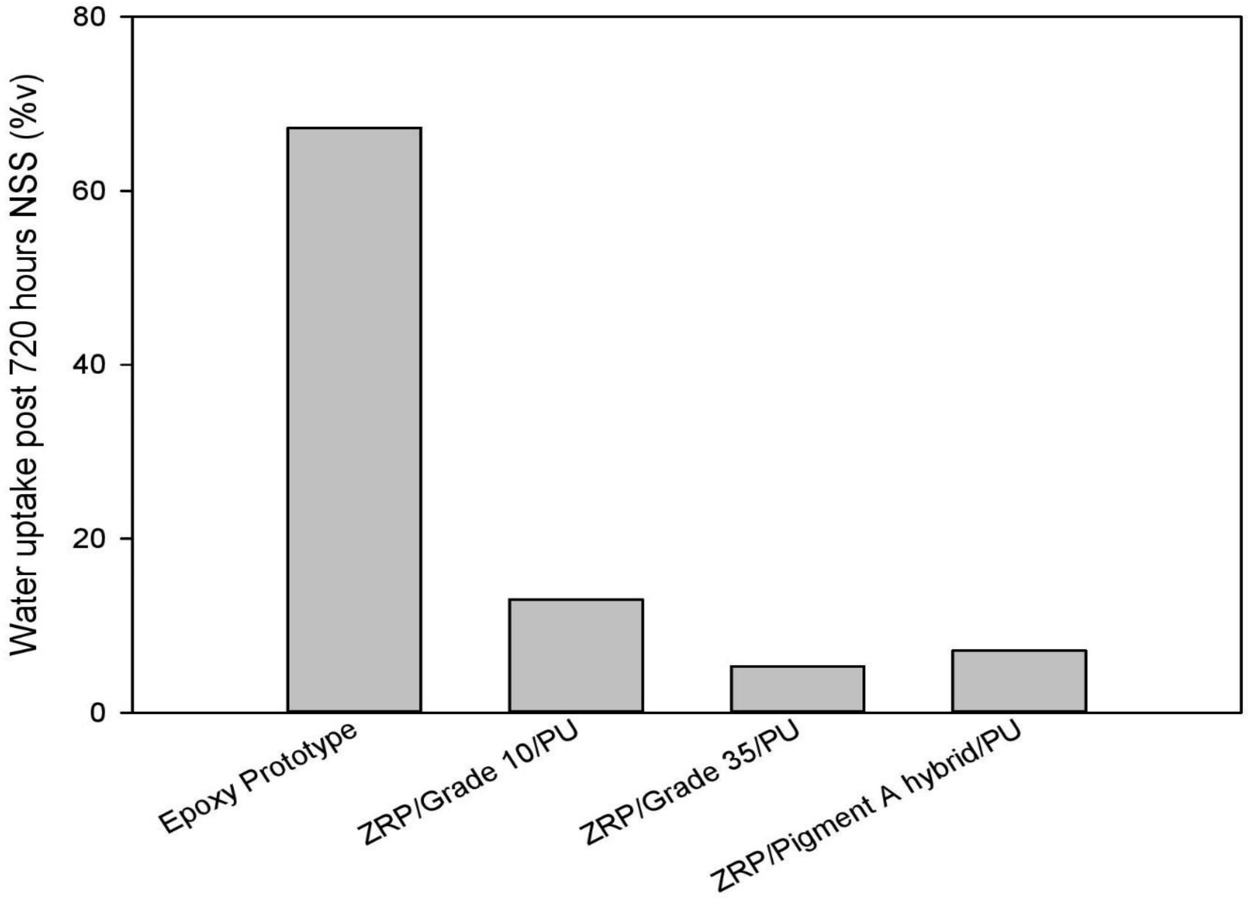
Graphene Enhanced Tiecoat



- Impedance measurements were carried out at 0, 72, 240,480 and 720 hours.
- All three graphene enhanced primers showed higher impedance values than the graphene-free control.
- Grade 35 in the intermediate layer showed significantly higher impedance.

Excellent protection
Good protection
Protection Begins
Poor protection

Water Uptake



- Water uptake values were extracted from the change in coating capacitance
- Coatings with a graphene enhanced tiecoat showed a significant reduction in water uptake.
- Coating Grade 35 had the lowest water uptake, which would infer the best barrier properties.

Graphene Enhanced Tiecoat

- After 1440 hours (C5 High testing requirement), the 3 coat systems showed no signs of blistering or corrosion development.
- The inclusion of graphene in the tiecoat resulted in improved barrier properties, evidenced by a reduction in water uptake and impedance values higher than the control.
- The combination of improved barrier protection offered by the graphene enhanced tiecoat combined with the sacrificial protection offered by the zinc rich primer is expected to further extend coating lifetime.
- Particularly high impedance values were observed with the use of Grade 35 as a 2nd Coat. This is likely an effect of the enhanced barrier properties in the tiecoat as demonstrated by the water uptake results.
- EIS data was able to differentiate between systems even though there was no visual difference.

Further Work

Further Work

- CX Environments
  - Ballast tank coatings
  - Universal primer systems
  - Suitable for full immersion
- Waterbased developments
  - To meet ongoing VOC legislative pressure
  - Waterbased DTM coating based on acrylic alkyd system
  - Primer based on epoxy / amine technology

Summary

- Graphene dispersions enable
    - Ease of use and incorporation
    - Minimised health and safety issues – encapsulated nanoplatelets
- The use of graphene dispersions has shown significant and repeatable improvements in anticorrosive performance, as demonstrated through *Salt Spray, EIS Testing and Water Vapor Transmission Rate Tests*.
- Improvements have been seen in single primer coats applied direct to the substrate and are translated into multilayer systems.
- Grade 35 graphene based coating showed exceptional performance on EIS and is expected to show extended system performance.
- It is likely that the combination of the sacrificial zinc rich layer and the barrier protection from the graphene enhanced coatings gives extended coating durability and lifetime.

Further info

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