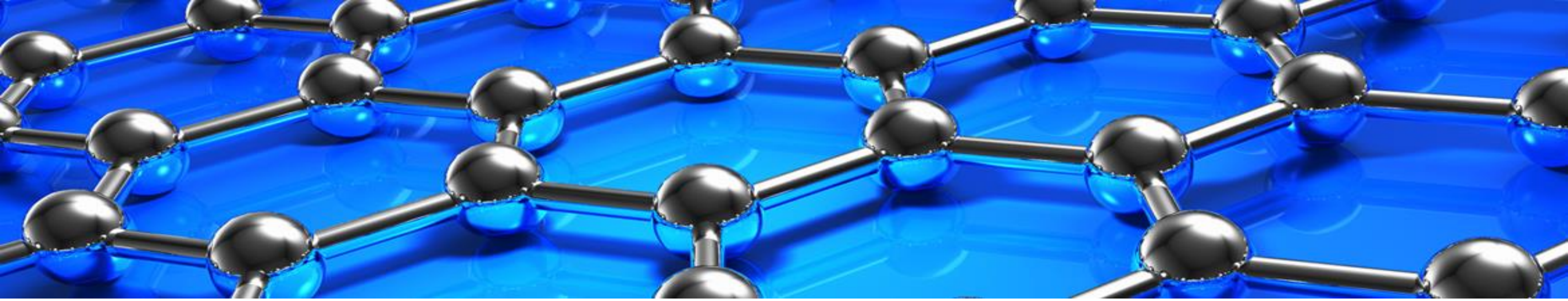
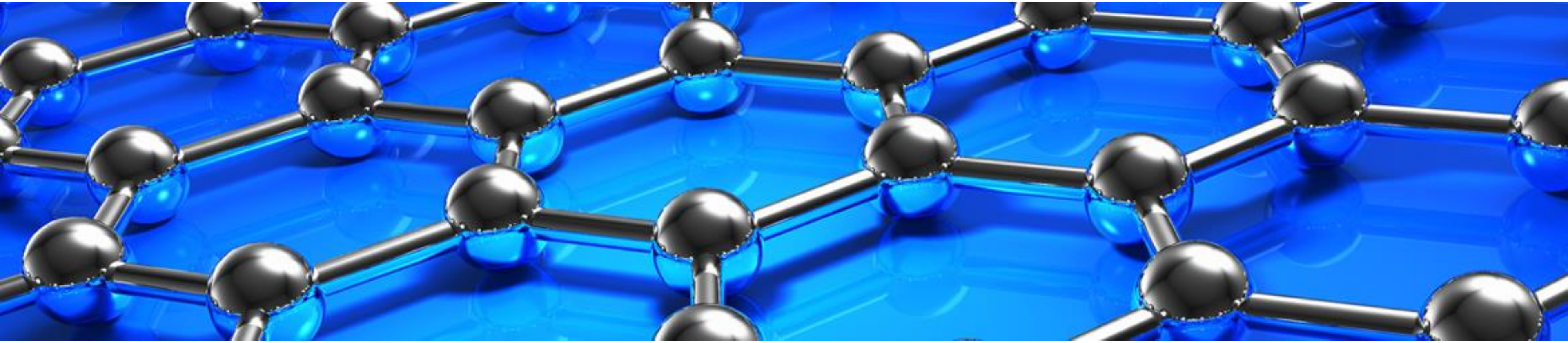


Applied Graphene Materials

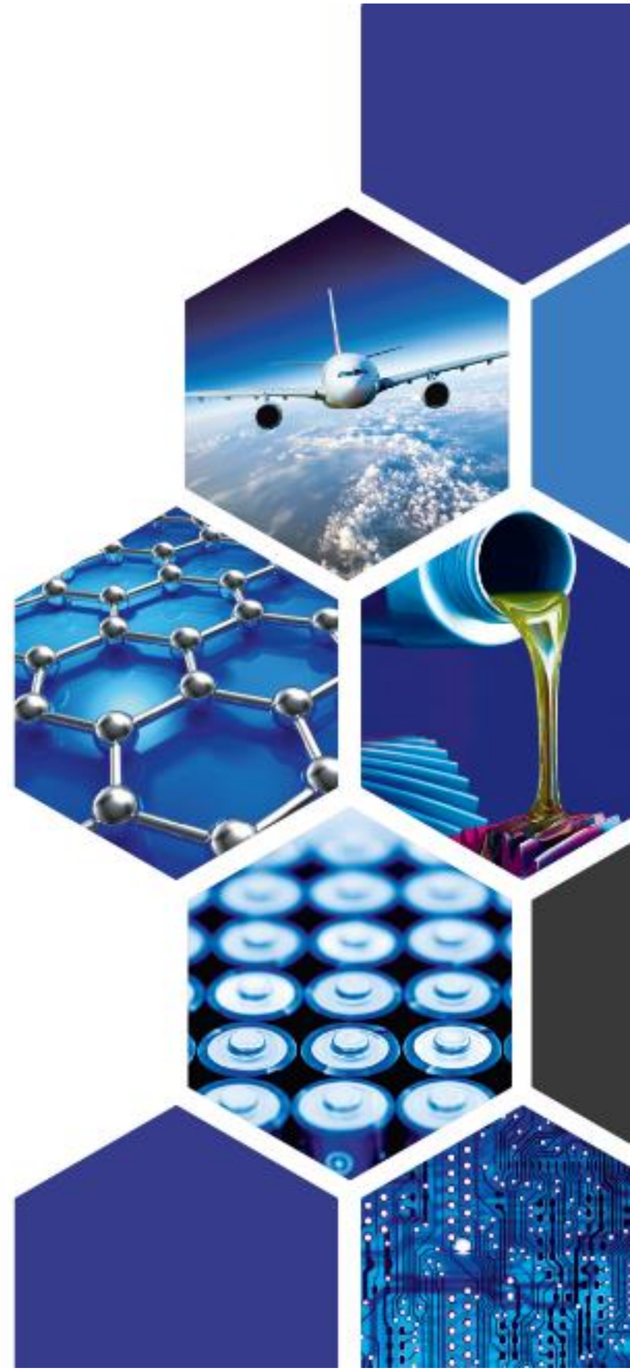
Characterization of a Novel Hybrid Anti-corrosive System Comprising Graphene Nanoplatelets and Non-Metal-containing Anti-corrosive Pigments

Andy Gent, William Weaver, Lynn Chikosha, Gaven Johnson & Matthew Sharp

March 2019



Introduction



Introduction

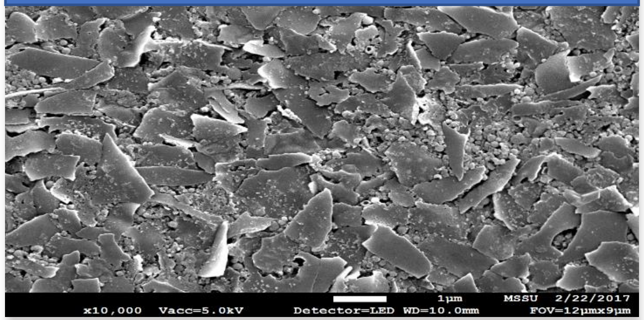
- **There are mixed literature reports of the use of graphene within anti-corrosive coatings**
  - **Corrosion performance enhancement or performance reduction?**
- **A variety of mechanisms have been proposed in the literature by which graphene delivers anti-corrosion performance**
  - **Physico-chemical process (restricting uptake of water/oxygen and salts)**
  - **Electro-chemical activity.**

Introduction

- **Platelike materials such as glass flake and micas have historically been used as barrier pigments that provide a tortuous path in anti-corrosion primers. Graphene offers a step change two-dimensional structure delivering:**
  - **high aspect ratio**
  - **high surface area**
  - **Low density**
- **Electro-chemical activity due to graphene's conductivity is dependent on**
  - **Graphene type**
  - **Loading level**
  - **Availability**
- **This work provides preliminary corrosion performance results relating to commercially available graphene nanoplatelet (GNP) products.**

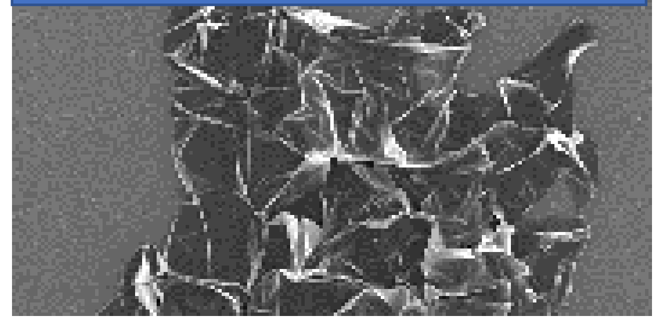
AGM Graphene Nano Platelets

Grade 10



- Reduced Graphene Oxide
- Composed of mixture of nanoplatelet type sheets

Grade 35



- Graphene
- Very thin, crumpled sheets (of 5-15 atomic layers)

AGM GNPs are manufactured using proprietary and patented bottom up synthesis

Graphene Dispersions

AGM supplies its graphenes in stable dispersions that are:

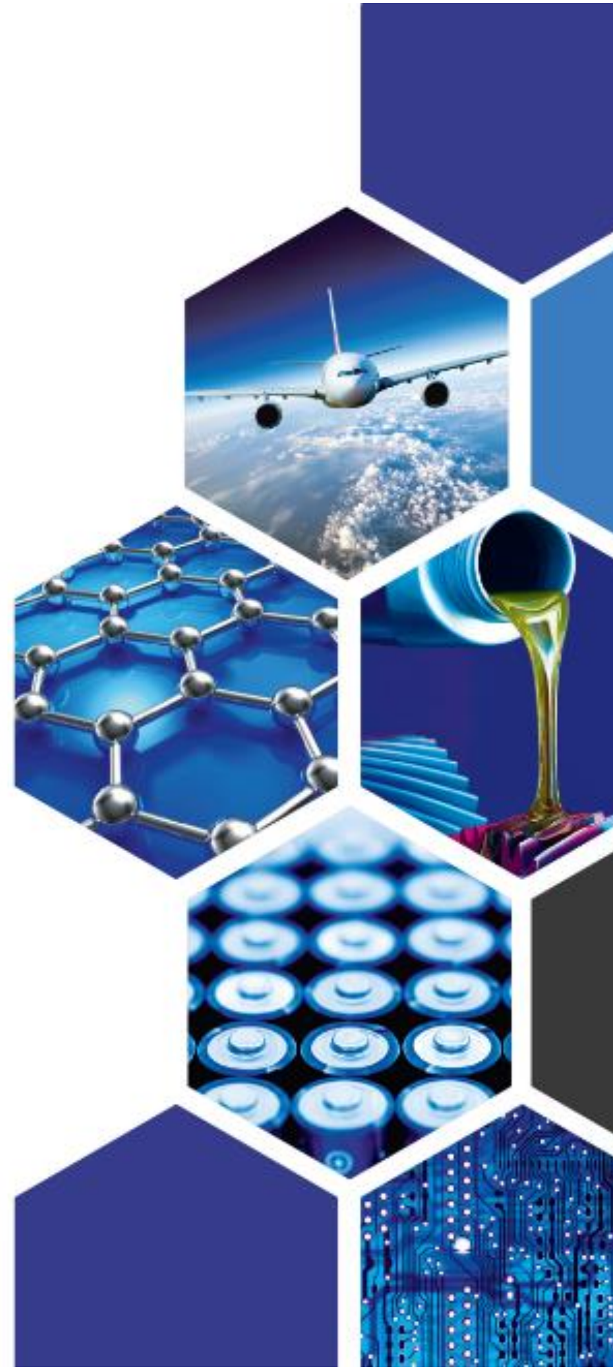
- Ready to use and easy to incorporate
- Available in a number of safe to handle formats
- Optimized to impart specific performance enhancements

Objectives

Demonstrate improved anti-corrosive performance

- Extended coating life expectancy
- Potential for reduced maintenance schedules
- Identify significant uplifts in anti-corrosion performance through synergistic use of non-metallic anti-corrosive pigments in combination with graphene nanoplatelets.
- Employing EIS as a tool to understand mechanism.
- Using commercially available and ready to use graphene dispersions, optimised for use in existing coatings systems.

Experimental



Test Program

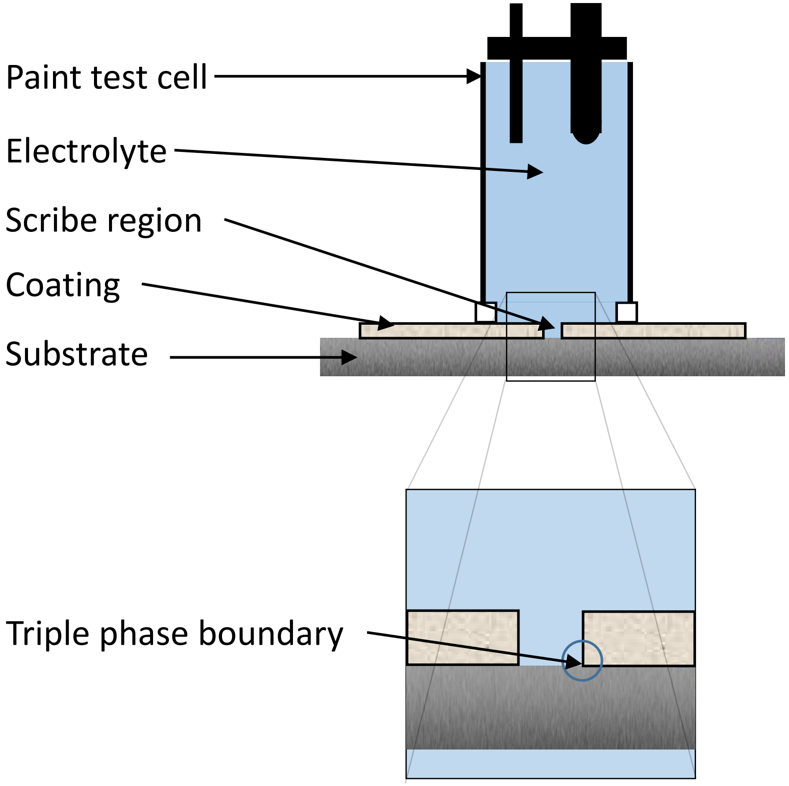
Demonstrating improved coating performance and extended lifetime in a typical Industrial Epoxy Formulation:

- Prohesion Testing
  - ASTMG85 annex 5
  - Duplicate panels were prepared for assessment at intervals of 500, 1000, 2000, 3000, and 5000 hours
- Electro-chemical studies
  - Novel Test Method looking at both scribed and unscribed substrates
  - AC Impedance Spectroscopy (AC EIS)
  - Corrosion Potential Measurements (E_{corr})
- Overcoating intervals and adhesion
- Water Vapor transmission (WVTR) Testing
- Mechanical Testing (Conical mandrel, Abrasion, Impact)

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).

Electro-chemical Study



- The EIS study of scribed samples provides supporting data relating to the barrier performance of the coatings
- Scribed samples were studied in addition to unscribed samples
  - Scribing offers an immediate study of the bare metal substrate in contact with electrolyte and functional coating (triple phase boundary)
  - To identify any electro-chemical influence imparted by the graphene and / or active inhibitor
  - Provides the opportunity to observe changes prior to the lengthy breakdown/degradation of the functional coating

Base Primer Formulation

Component	Weight percent
Epoxy (Liquid Epoxy Resin, EEW = 250)	15.119
Amino resin	0.244
Dispersant	0.402
Xylene	15.376
Bentonite thixotrope	0.366
Butanol	1.986
Xylene	10.966
Titanium Dioxide	10.966
Anticorrosive Pigment	4-8 (Variable)
Blanc Fixe	43.619
GNP Dispersion	**0-10 (Variable)**
Epoxy	**0-10 (Variable)**
Xylene	0

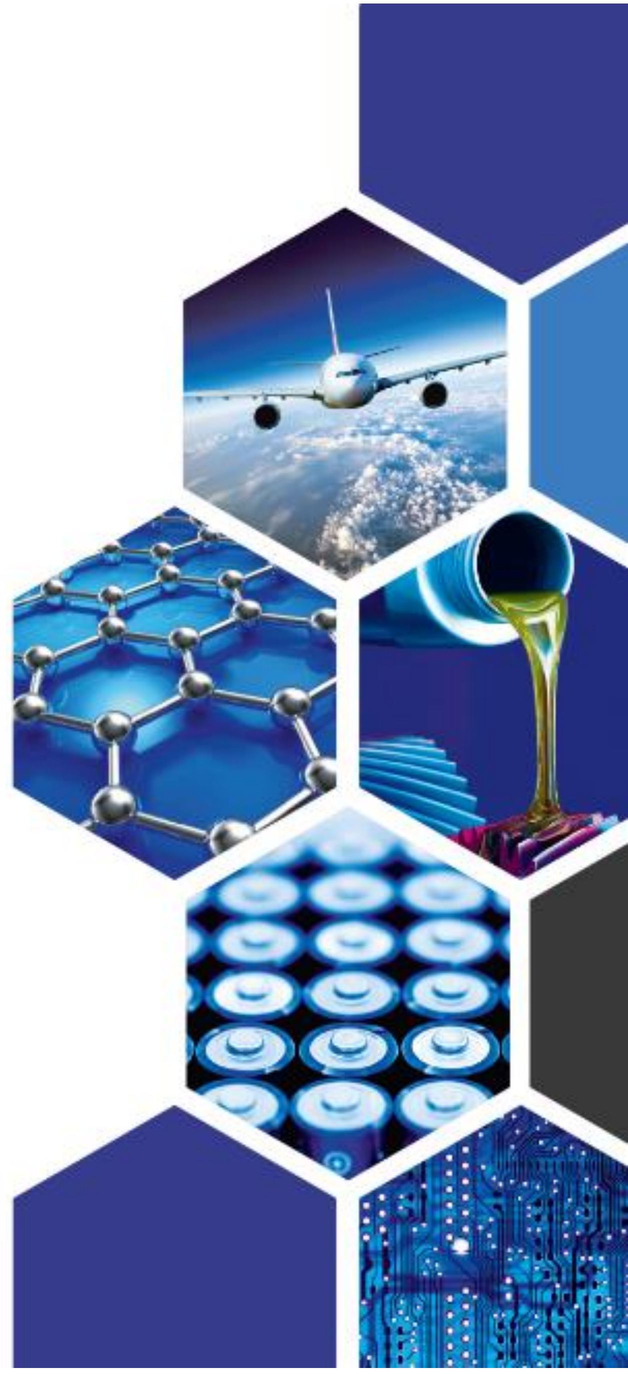
VOC	320 g/l
PVC	35%
Stoichiometry	100%
Hardener	Polyamine

Primer Formulation Variants

Variant	Description	GNP Content
1	Standard	None
2	Standard + 8% $Zn_3(PO_4)_2$	None
3	Standard + 4% $Zn_3(PO_4)_2$	None
4	**Standard + Pigment A***	None
5	Standard	Grade 10 at 0.5%
6	Standard + 8% $Zn_3(PO_4)_2$	Grade 10 at 0.5%
7	Standard + 4% $Zn_3(PO_4)_2$	Grade 10 at 0.5%
8	**Standard + Pigment A***	Grade 10 at 0.5%
9	Standard	Grade 35 at 0.1%
10	Standard + 8% $Zn_3(PO_4)_2$	Grade 35 at 0.1%
11	Standard + 4% $Zn_3(PO_4)_2$	Grade 35 at 0.1%
12	**Standard + Pigment A**	Grade 35 at 0.1%

*Calcium oxide-modified silica (non-metallic anti-corrosive pigment)

Results



Prohesion Testing – 1000 Hours

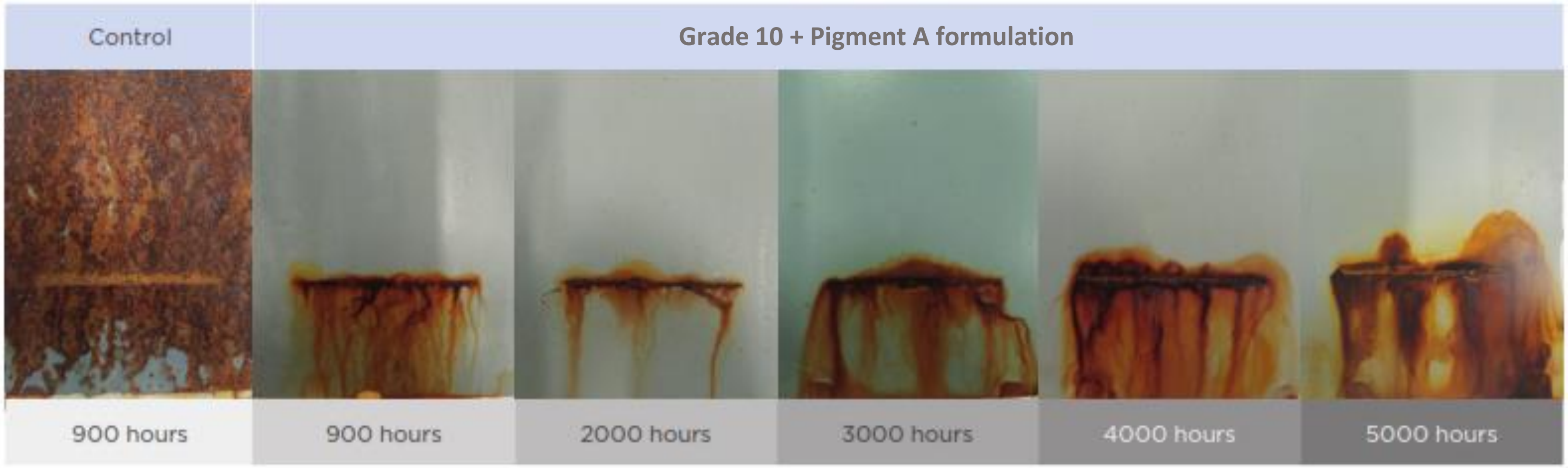
Primary Anti-corrosive	GNP Content	Creep (mm)	Blistering Quantity	Size (ISO)	Corrosion	Comments
None	None	>10	0	S0	Ri5	Very poor
None	Grade 10 at 0.5%	>10	0	S4	Ri5	Corroded across whole face
None	Grade 35 at 0.1%	3	0	S0	Ri3	Corrosion spotting across face
8% $Zn_3(PO_4)_2$	None	4	1	S3	Ri5	Corrosion across face
8% $Zn_3(PO_4)_2$	Grade 10 at 0.5%	2	0	S0	Ri1	Corrosion spotting across face
8% $Zn_3(PO_4)_2$	Grade 35 at 0.1%	2	0	S0	Ri2	Corrosion spotting across face
4% $Zn_3(PO_4)_2$	None	8	1	S3	Ri5	Corrosion across face
4% $Zn_3(PO_4)_2$	Grade 10 at 0.5%	4	0	S0	Ri0	Good
4% $Zn_3(PO_4)_2$	Grade 35 at 0.1%	>10	0	S0	Ri5	Completely corroded
Pigment A	None	3	0	S0	Ri3	Corrosion spots starting
Pigment A	Grade 10 at 0.5%	1	0	S0	Ri2	Good
Pigment A	Grade 35 at 0.1%	>10	3	S4	Ri5	Corroded across whole face

Prohesion Testing – 5000 Hours

Primary Anti-corrosive	GNP Content	Creep (mm)	Blistering Quantity	Size (ISO)	Corrosion	Comments
None	None	>10	0	S0	Ri5	Very poor
None	Grade 10 at 0.5%	>10	0	S4	Ri5	Corroded across whole face
None	Grade 35 at 0.1%	>10	0	S0	Ri5	Corrosion spotting cross face
8% $Zn_3(PO_4)_2$	None	>10	1	S3	Ri5	Corrosion across face
8% $Zn_3(PO_4)_2$	Grade 10 at 0.5%	>10	0	S0	Ri5	Corrosion spotting cross face
8% $Zn_3(PO_4)_2$	Grade 35 at 0.1%	>10	0	S0	Ri5	Corrosion spotting cross face
4% $Zn_3(PO_4)_2$	None	>10	1	S3	Ri5	Corrosion across face
4% $Zn_3(PO_4)_2$	Grade 10 at 0.5%	5	1	S2	Ri2	Corrosion spreading from scribe
4% $Zn_3(PO_4)_2$	Grade 35 at 0.1%	>10	0	S0	Ri5	Completely corroded
Pigment A	None	>10	0	S0	Ri5	Corrosion spots starting
Pigment A	Grade 10 at 0.5%	1	0	S0	Ri2	Good
Pigment A	Grade 35 at 0.1%	>10	3	S4	Ri5	Corroded across whole face

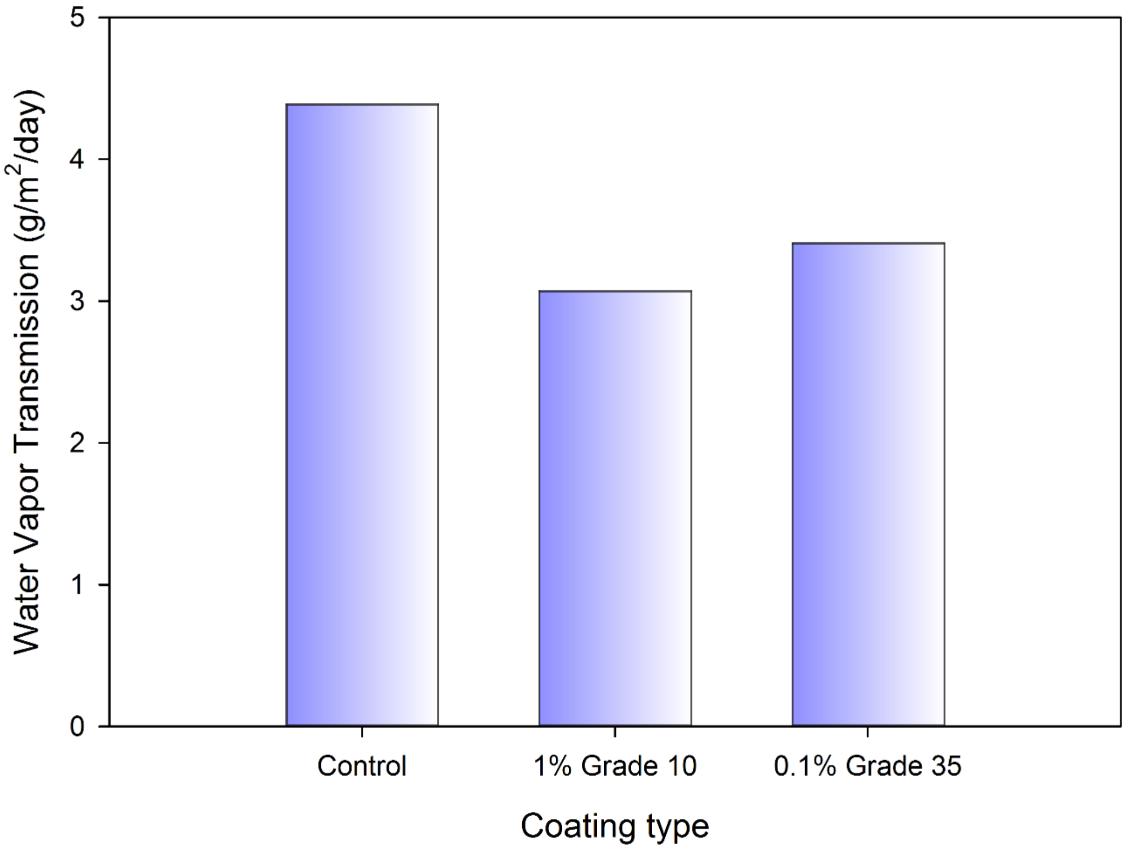
Prohesion Test Sample Images

- Performance on ASTM G85 prohesion test was extended from 1000 to 5000 hours by using graphene in combination with metal free active inhibitors



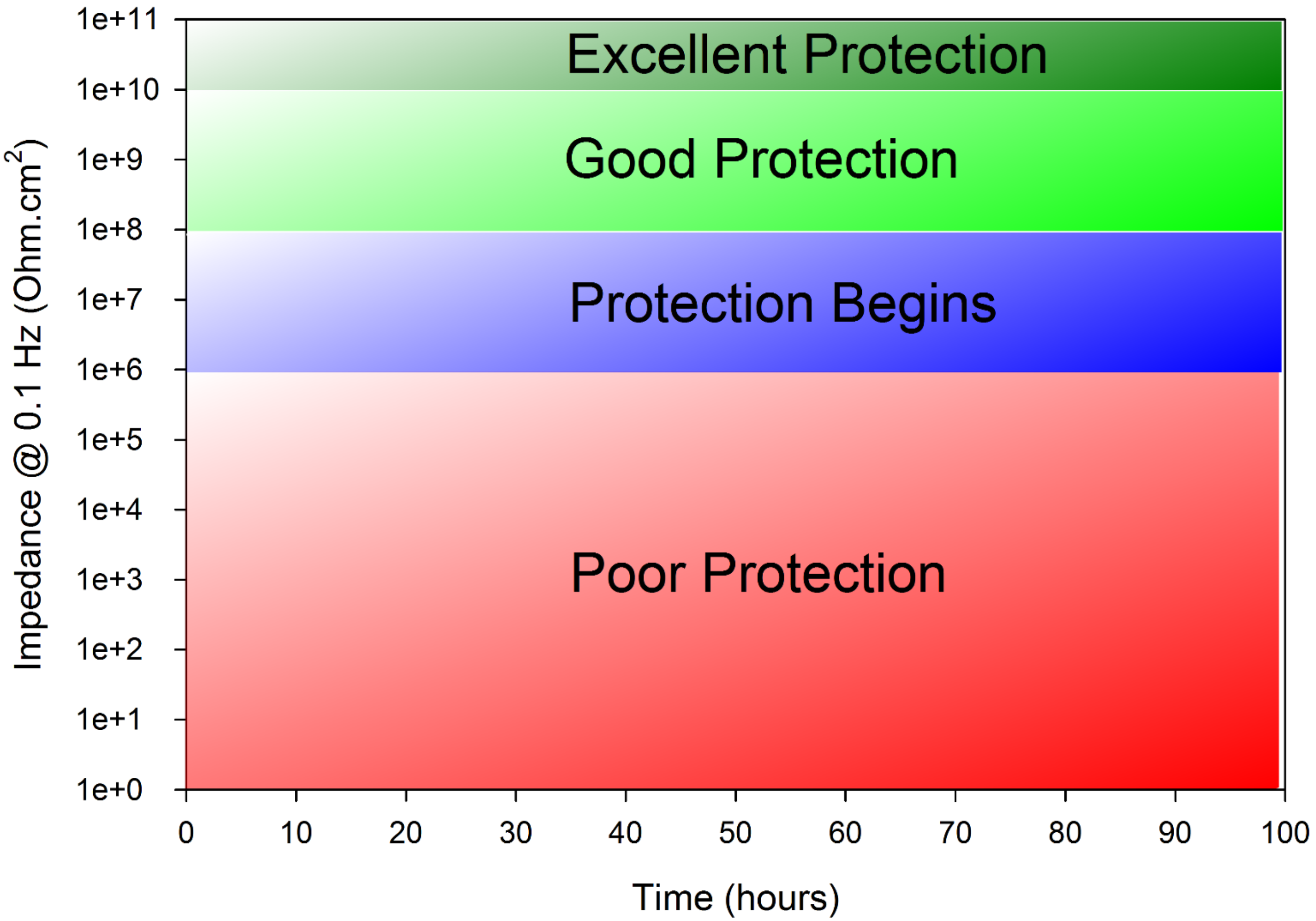
- Testing using ASTM G85 Prohesion allows for stronger correlation with natural exposure, as opposed to ASTM B117 (Continuous Salt Spray).
- Further work is currently underway looking at performance under Continuous Salt Spray.

Water Vapor Transmission (WVTR)

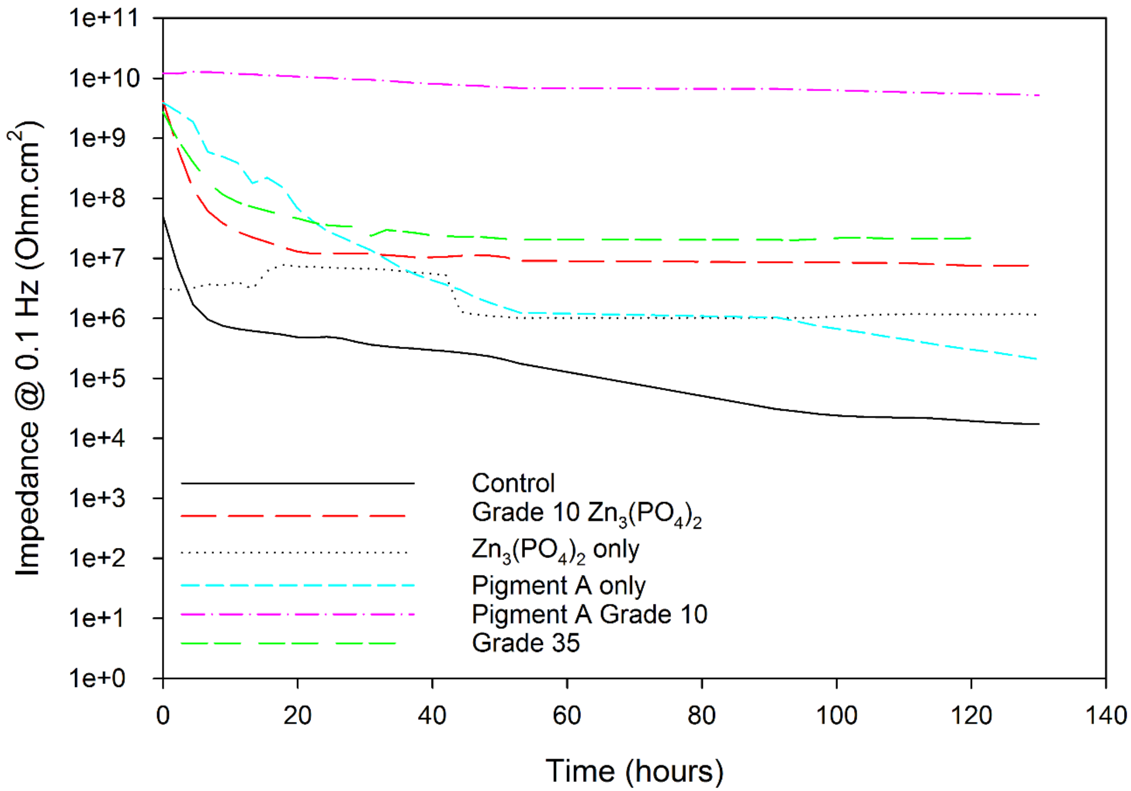


- ASTM D 1653-03 using Test Method B (wet cup method)
- The WVTR of the Control primer with grade 10 at 0.1 wt.% loading was found to be the lowest
  - Best barrier property performance increase
  - 30% reduction in WVTR
- Grade 35 at 0.1 wt.% loading gave a 22% reduction in in WVTR

AC Impedance (EIS) of Coatings



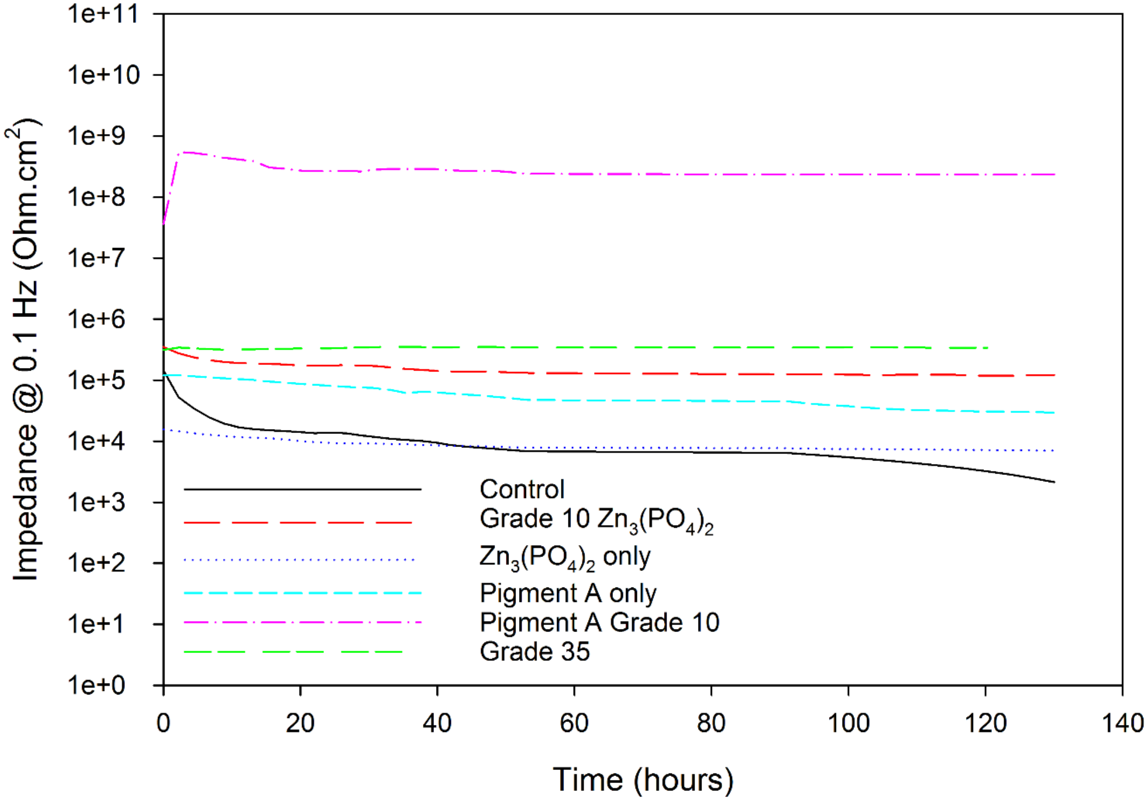
Impedance Testing (EIS) – Unscribed Coatings



- Graphene modified coatings offered a higher impedance values than straight $Zn_3(PO_4)_2$ and Pigment A samples
- Increase in impedance observed above $Zn_3(PO_4)_2$ base in Grade 10 $Zn_3(PO_4)_2$ hybrid sample
- Excellent (10^{10} Ohm.cm^2) impedance observed with Grade 10 with Pigment A coating over duration of test.

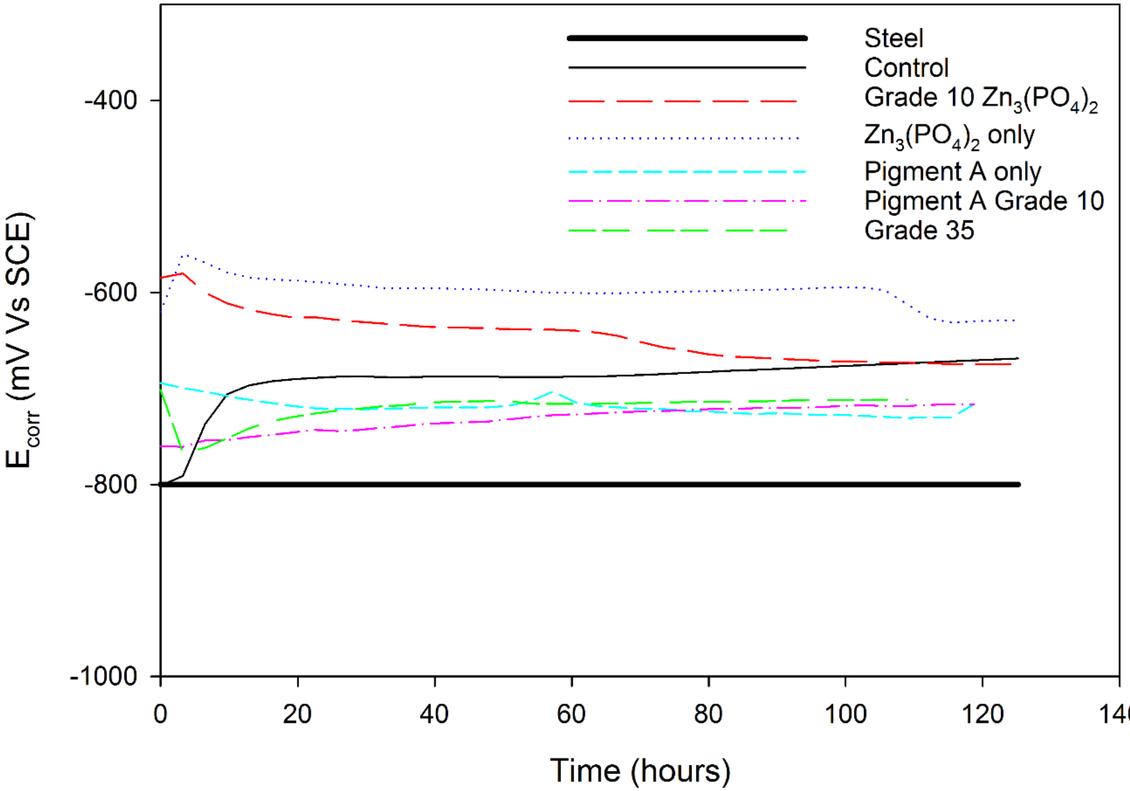
Increased impedance equals better barrier.

Impedance Testing (EIS) – Scribed Coatings



- Coatings in general are of 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
  - Continued performance barrier effect with coatings incorporating GNPS
- Pigment A shows a higher level of impedance compared to $Zn_3(PO_4)_2$
- Grade 10/Pigment A hybrid continues to show significant performance increase in contrast to $Zn_3(PO_4)_2$ hybrids

Corrosion Potential Measurements – Scribed Coatings



- Scribing significantly reduced the ECorr, as expected
- Both $Zn_3(PO_4)_2$ sample and Grade 10 $Zn_3(PO_4)_2$ samples show initial elevated but decreasing E_{corr} values
  - Solubility is higher compared to Pigment A
  - Faster active utilization
- Pigment A + Grade 10 shows a steady increase in corrosion potential
- Initial testing only conducted over a relatively short time period

Mechanical Properties

		Flexibility		Abrasion Resistance	Impact Resistance
Description	GNP Content	Cracking (mm)	Elongation (%)	Wear Rating	Cracking begins at height
None	None	0	<35	389	20cm
None	Grade 10 at 0.5%	120	3	460	10cm
None	Grade 35 at 0.1%	12	19	539	10cm
8% $Zn_3(PO_4)_2$	None	4	21	347	20cm
8% $Zn_3(PO_4)_2$	Grade 10 at 0.5%	4	21	534	50cm
8% $Zn_3(PO_4)_2$	Grade 35 at 0.1%	4	21	269	10cm
4% $Zn_3(PO_4)_2$	None	4	21	356	10cm
4% $Zn_3(PO_4)_2$	Grade 10 at 0.5%	6	23	280	60cm
4% $Zn_3(PO_4)_2$	Grade 35 at 0.1%	100	5	365	30cm
Pigment A	None	120	3	297	10cm
Pigment A	Grade 10 at 0.5%	120	3	397	10cm
Pigment A	Grade 35 at 0.1%	11	19	362	10cm

Overcoat Interval/Adhesion

			Initial		Wet		Recovery	
1st Coat	2nd Coat	Overcoating Interval	Intercoat Adhesion	Substrate Adhesion	Intercoat Adhesion	Substrate Adhesion	Intercoat Adhesion	Substrate Adhesion
Control	Topcoat	1 day	4	5	4	5	5	4
Control	Topcoat	3 day	4	5	4	5	5	4
Control	Topcoat	7 day	4	5	5	4	4	4
Control + Grade35	Topcoat	1 day	4	5	4	5	5	4
Control + Grade35	Topcoat	3 day	4	5	4	5	5	4
Control + Grade10	Topcoat	1 day	5	5	5	4	5	4
Control + Grade10	Topcoat	3 day	5	5	5	4	4	4
Control + Grade10	Topcoat	7 day	5	5	4	5	4	4

- All systems showed good to excellent adhesion to substrates
- Good overcoatability with PU topcoat, intervals up to 7 days.

Discussion

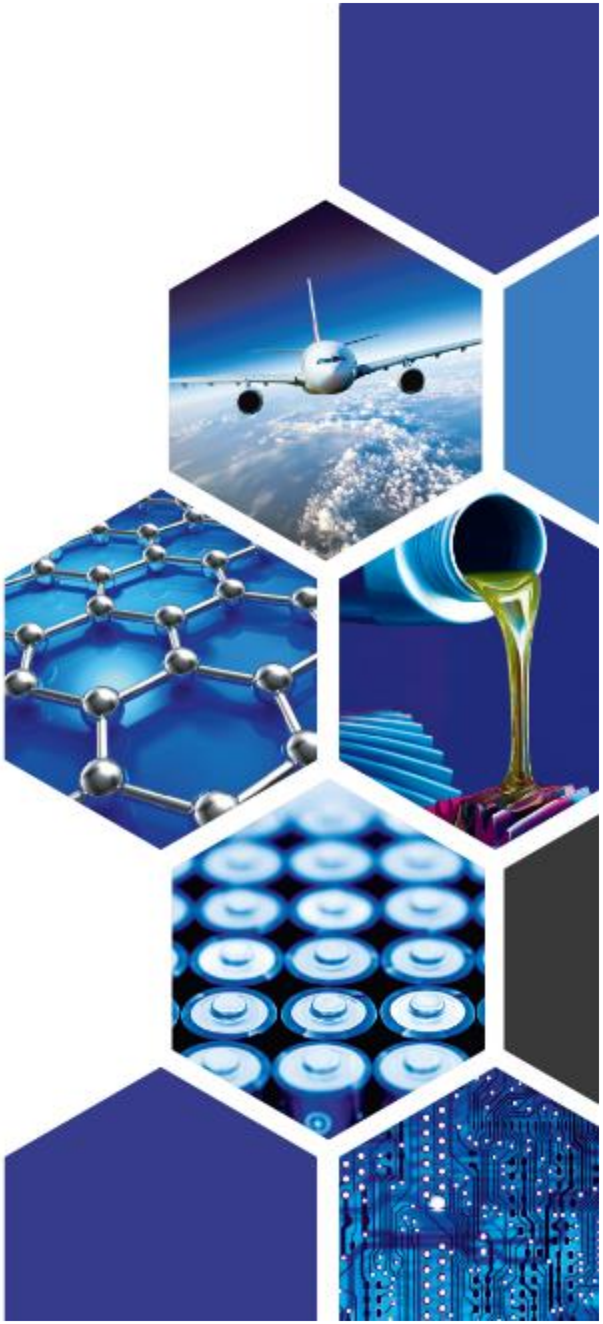
- GNP incorporated into the base primer alone or combined with an active pigment (hybrid) improved the barrier/corrosion properties of the coatings
  - Grade 10 GNPs combined with active pigments offer high level of performance. No apparent evidence of electro-chemical contribution to corrosion resistance
  - Grade 10 (reduced graphene oxide) has a relatively high electrical resistance where Grade 35 (graphene) is more electrically conductive (both systems are loaded substantially below the percolation threshold)

Discussion

- The primary mechanism of the GNP suggested is physico-chemical, extending the diffusional pathway (tortuous path).
- Assuming that film formation and hydrophilic pathways are unchanged (Pigment Volume Concentration constant)
- The net effect an efficient physico-chemical barrier effect to water/salts is
    - steeper decrease in water concentration through the film.
    - preservation of the active pigment over the coating life
- Such a mechanism would be a function of
    - Physico-chemical impact of the graphene,
    - graphene morphology
    - solubility and passivation rate of the active pigments.
- Additional studies are required to fully determine the exact mechanism of the enhanced performance, which is observed in the salt spray resistance.

Conclusion

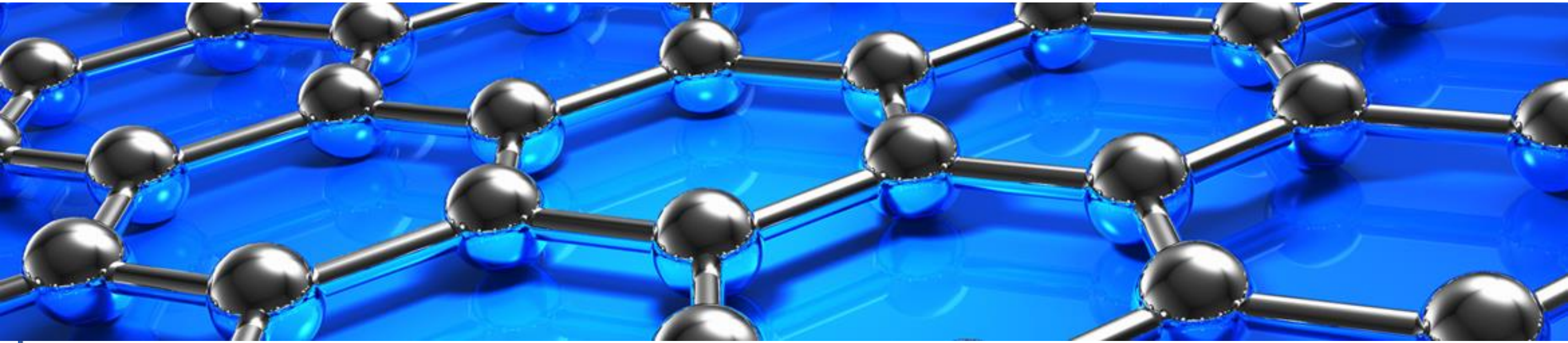
- Graphene modified hybrid coatings offered
  - Good over-coatability
  - Good adhesion
  - Significantly extended corrosion resistance under prohesion
- Graphene modified hybrids provide opportunity for
  - Reduced maintenance costs
  - Extended maintenance intervals
  - Green alternative to zinc phosphate through combination with Pigment A



Applied Graphene Materials

www.appliedgraphenematerials.com
info@appliedgraphenematerials.com

The Innovation Centre,
Wilton Site,
Redcar.
TS10 4RF
United Kingdom



…Graphene in products used by everybody, everyday