Applied Graphene Materials

Corrosion: Meeting Tomorrows Performance Needs with Graphene Nano-Platelets

Western Coatings Show

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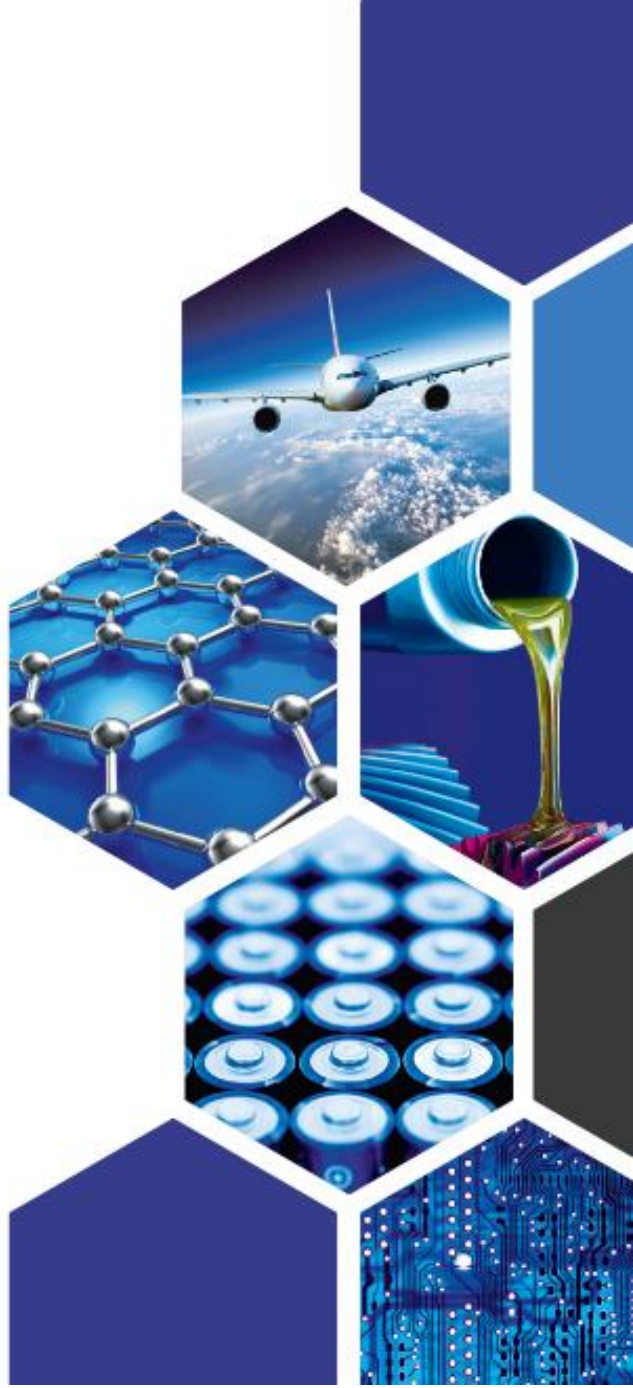
Introduction



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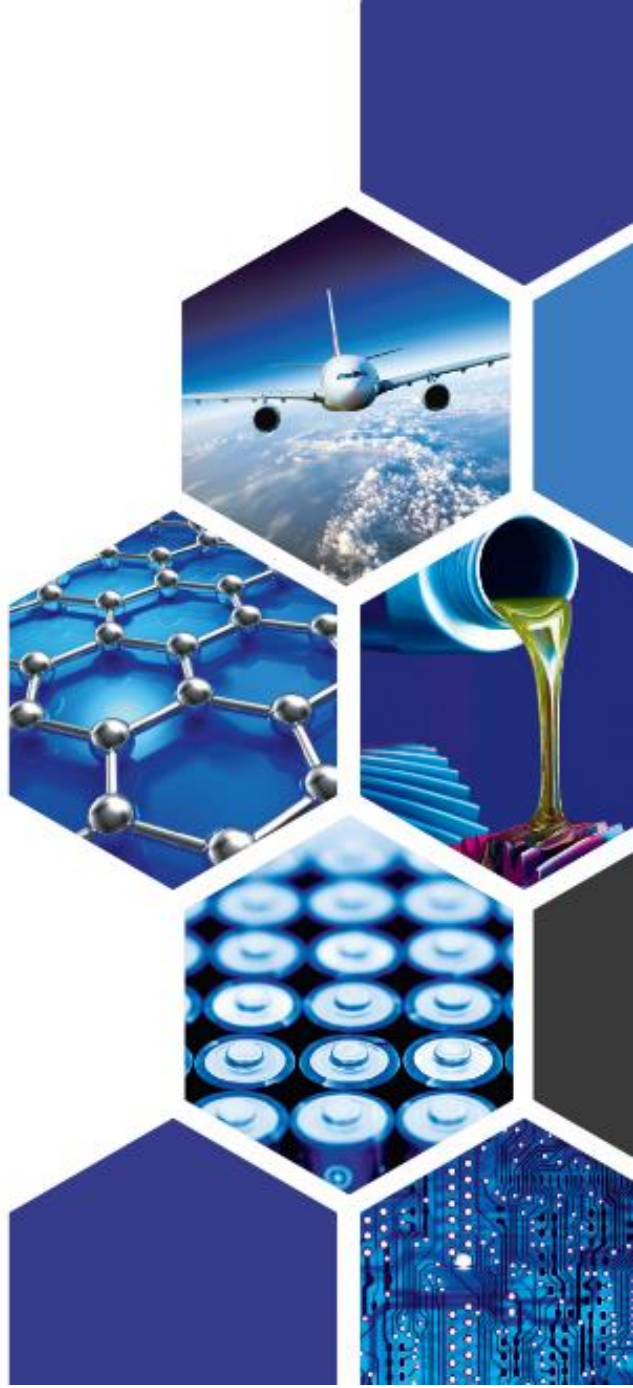
Introduction

- There are mixed literature reports of the use of Graphene within anticorrosive coatings
  - Corrosion performance enhancement or performance reduction?
- A variety of mechanisms have been proposed in the literature by which Graphene delivers anticorrosion performance
  - Physiochemical process (restricting uptake of water, oxygen and salts)
  - Electrochemical activity.



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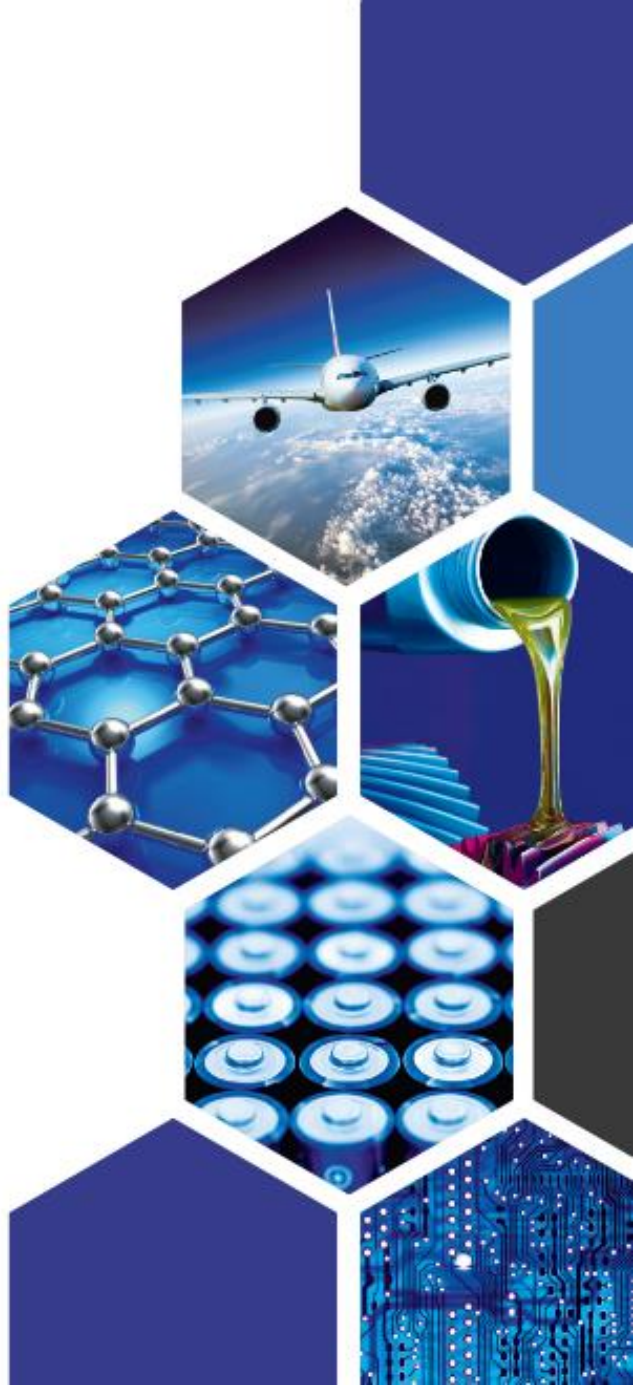
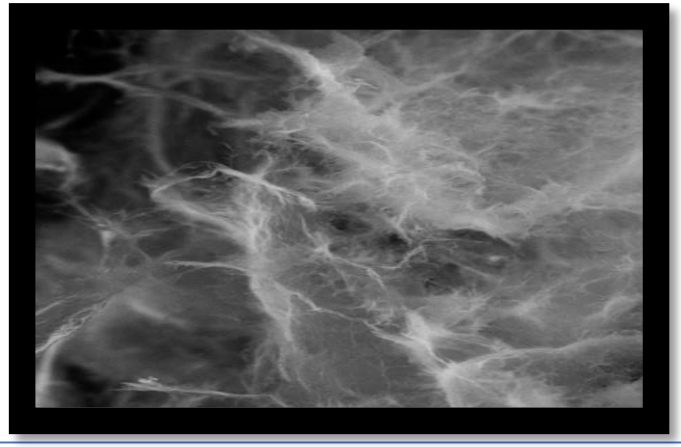
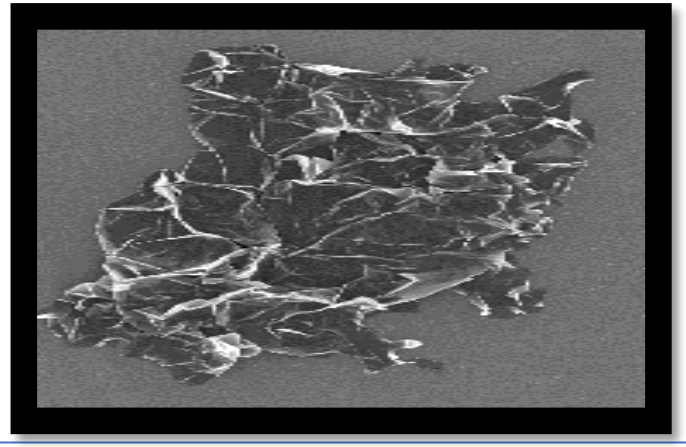
Introduction

- Plate-like materials such as glass flake and micas have been used as barrier pigments to provide a tortuous path in anticorrosion primers.
- Graphene offers a step change two-dimensional structure delivering:
  - High aspect ratio
  - High surface area
  - Low volume density
- Electrochemical activity due to Graphene's conductivity is dependent on:
  - Graphene type
  - Loading level
- This work provides preliminary corrosion performance results relating to commercially available Graphene nanoplatelet (GNP) products.



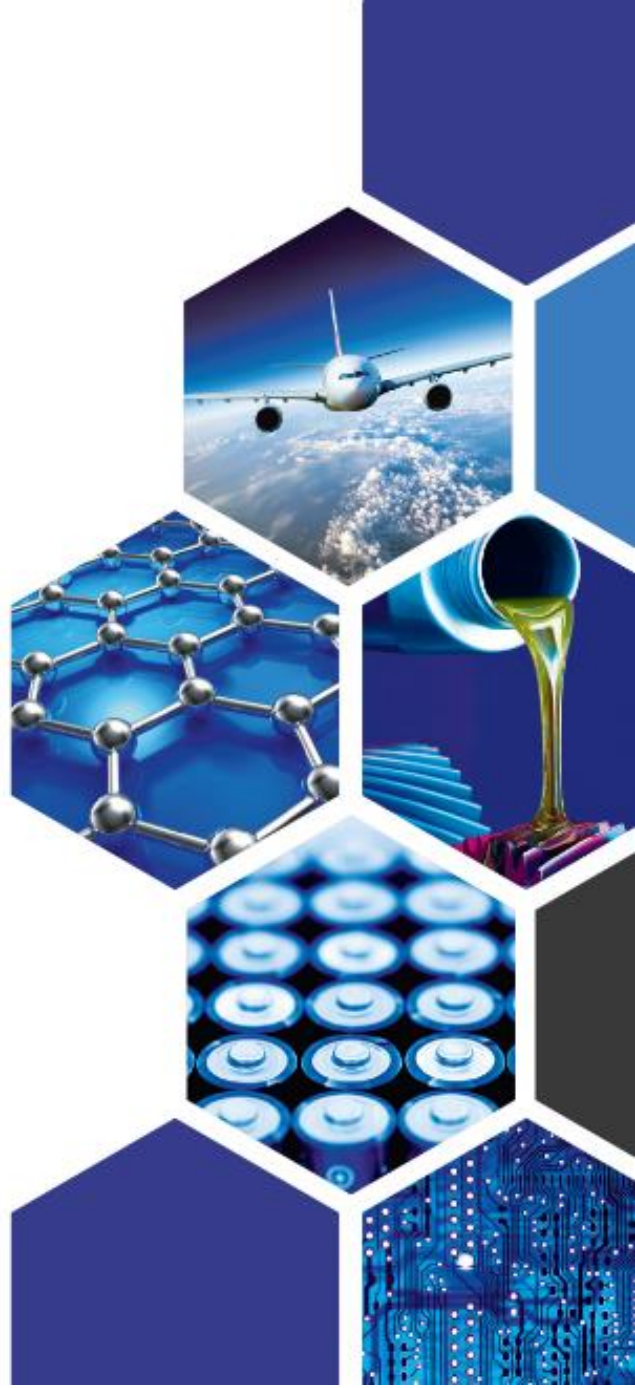
AGM Graphene Nano-Platelets





Graphene Nano-Platelets – AGNP-35

- AGM GNPs are manufactured using proprietary and patented bottom up synthesis process
- Graphene, composed of very thin, crumpled sheets, typically 5-7 atomic layers with approximately 5% oxygen
- Very low density and high surface area, enabling enhanced corrosion resistance at very low loadings.
- Recommended active Graphene addition between 0.025% to 0.1% weight of total paint formulation



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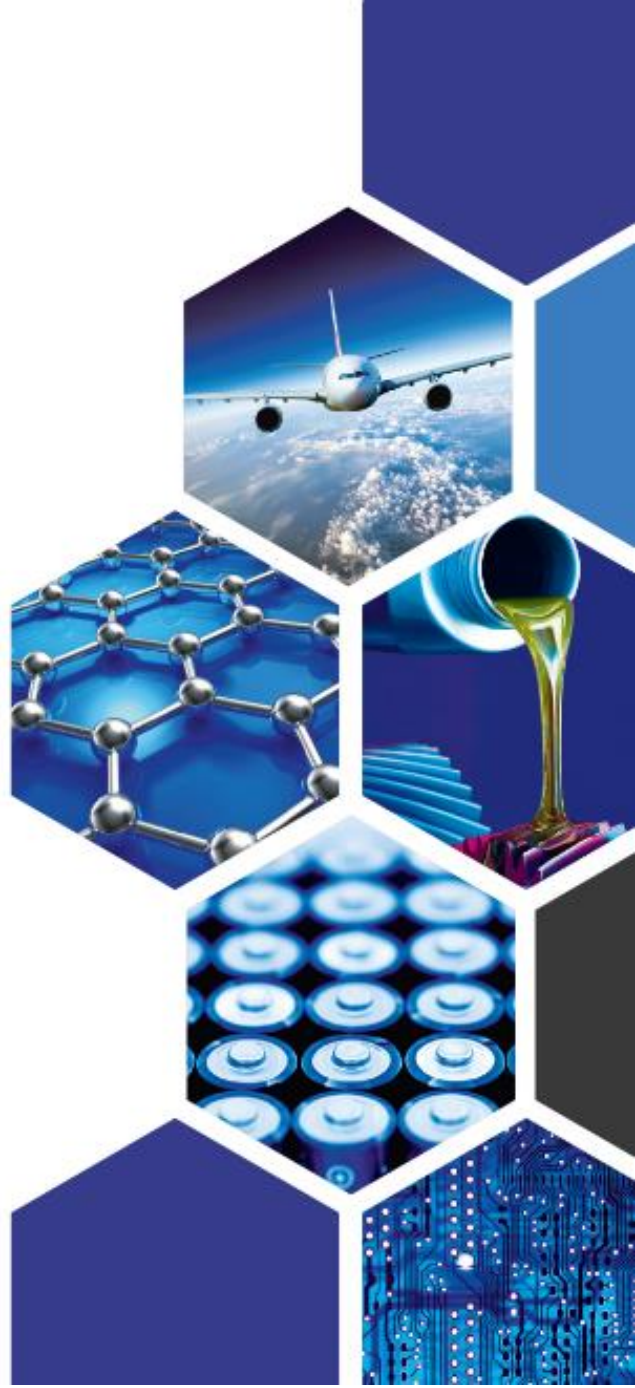
Delaying Time to Corrosion Onset

Impact of Corrosion…

- In the US alone, it's estimated to cost over $450bil/yr, or nearly 3% of GDP
- Estimates suggest that the total cost of corrosion globally to $2.5trillion/yr

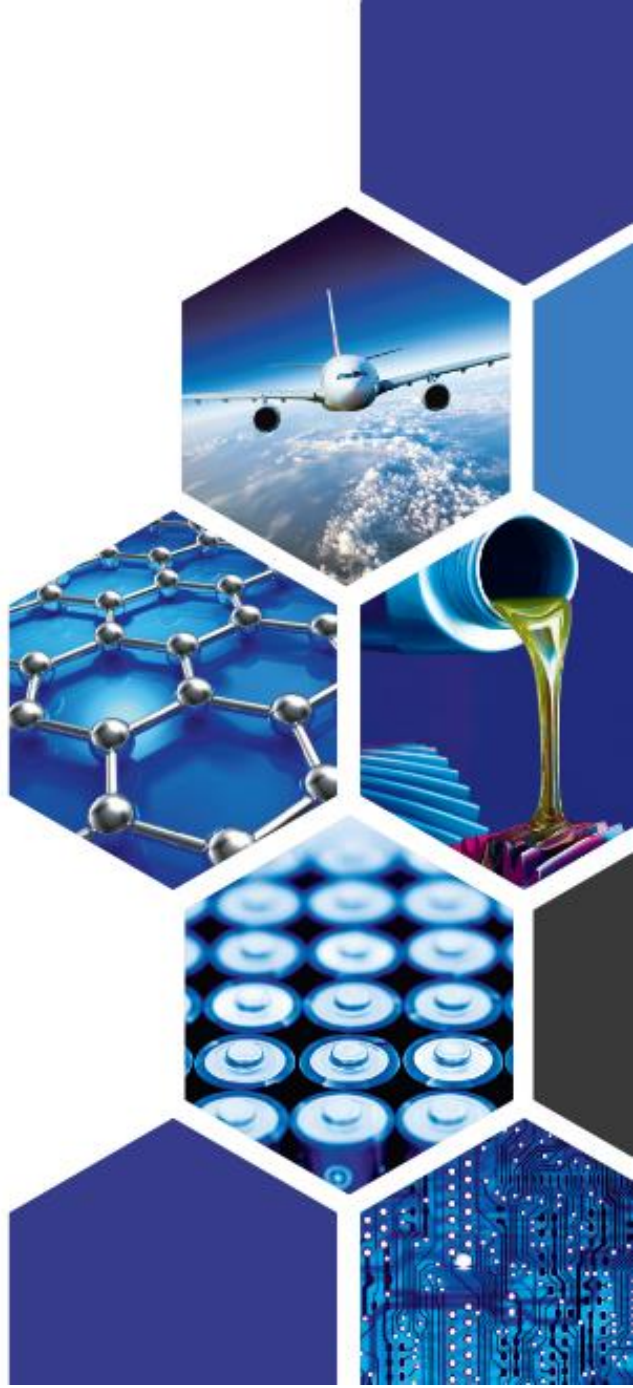
Economic Regions	Agriculture CoC US$ billion	Industry CoC US$ billion	Services CoC US$ billion	Total CoC US$ billion	Total GDP US$ billion	CoC % GDP
United States	2.0	303.2	146.0	451.3	16,720	2.7%
India	17.7	20.3	32.3	70.3	1,670	4.2%
European Region	3.5	401	297	701.5	18,331	3.8%
Arab World	13.3	34.2	92.6	140.1	2,789	5.0%
China	56.2	192.5	146.2	394.9	9,330	4.2%
Russia	5.4	37.2	41.9	84.5	2,113	4.0%
Japan	0.6	45.9	5.1	51.6	5,002	1.0%
Four Asian Tigers + Macau	1.5	29.9	27.3	58.6	2,302	2.5%
Rest of the World	52.4	382.5	117.6	552.5	16,057	3.4%
Global	**152.7**	**1446.7**	**906.0**	**2505.4**	**74,314**	**3.4%**



Delaying Time to Corrosion Onset

Target Benefits…

- **Improved coating durability and time to corrosion onset.**
- **Extension of coating life allowing increased time between maintenance intervals.**
- **Significant reduction in repair and re-paint costs over the lifetime of the coating**
- **Potential to reduce coating complexity as well as number of layers in a system**



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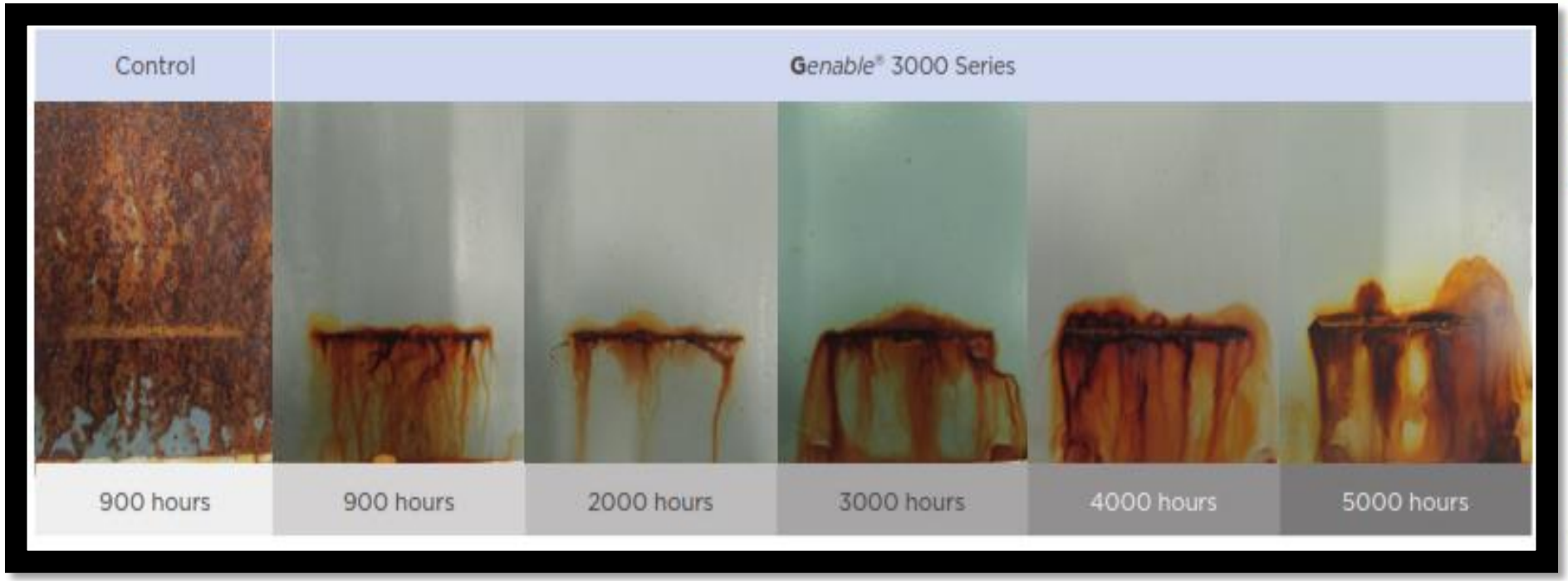
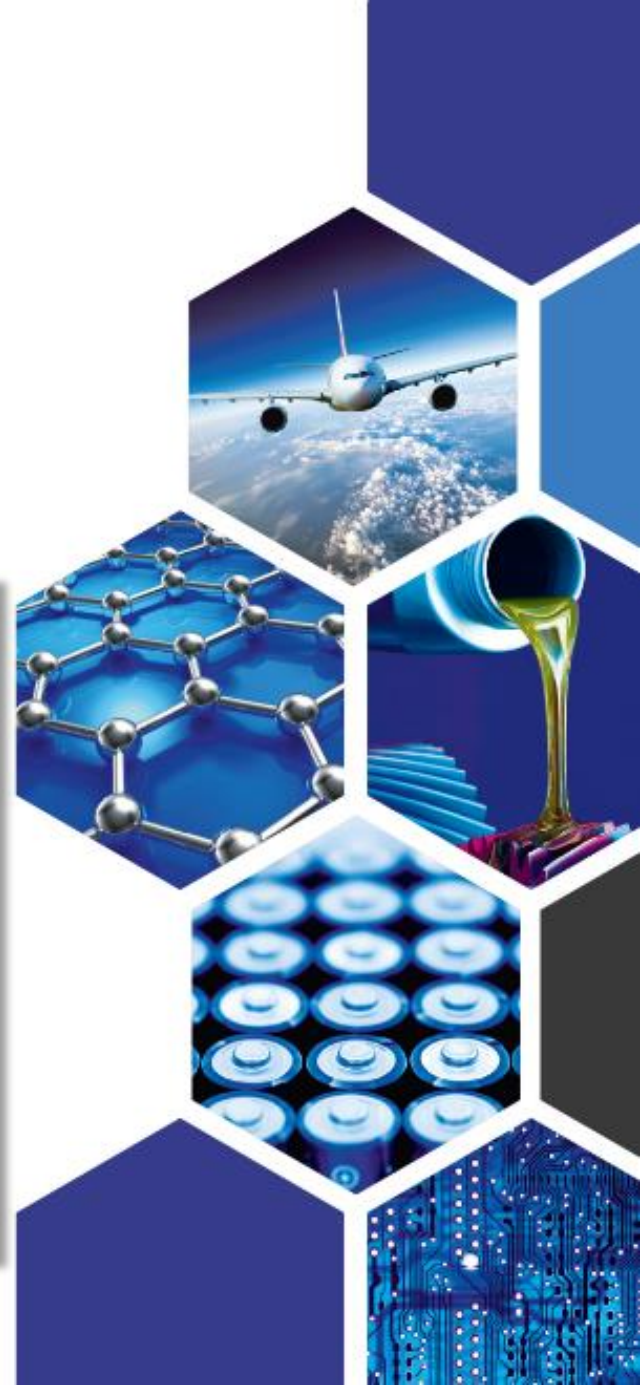
Previous Investigation in Anti-Corrosion

Previously, AGM has developed and reported meaningful anticorrosive performance gains in solvent based systems.

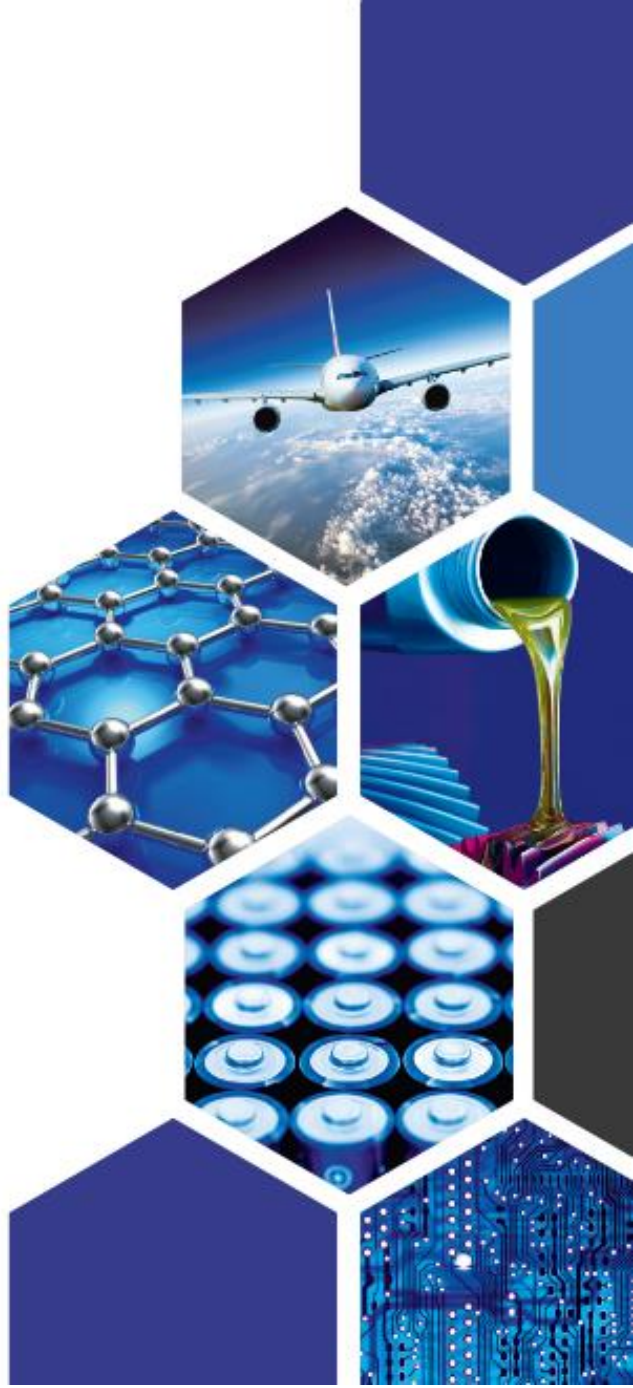
- **For example, performance of a standard industrial primer was extended from less than 1000 hours to over 5000 hours (Prohesion Testing) with the addition of G*enable*® 3000, a graphene based metal free active anti-corrosion additive.**





Project Objectives

- To demonstrate compatibility of the graphene dispersion with standard industrial water based coating formulations
- Develop further understanding of the mechanisms of protection
- Identify a significant uplift in anti-corrosion performance through the incorporation of a graphene nanoplatelet dispersion in to water based industrial coatings



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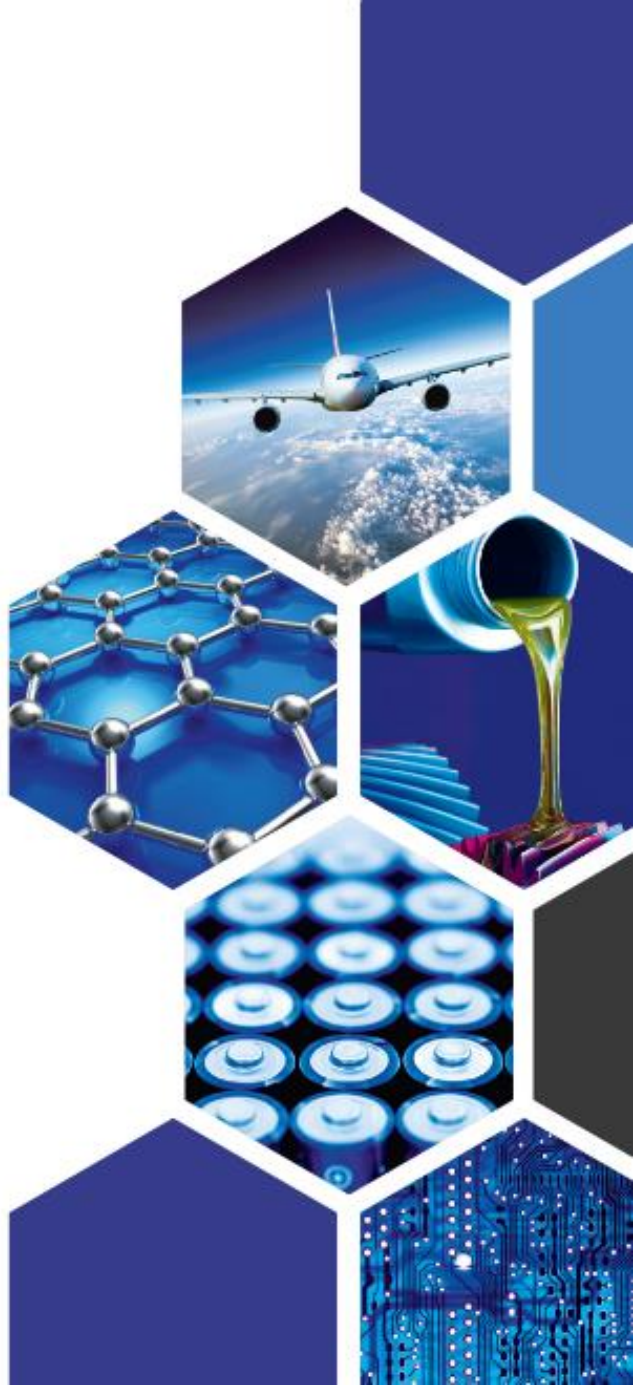
Genable® 1250 – Water Based Graphene Dispersion

- Development of water based coatings remains a focus for industry formulators.
- Driven by the continuing tightening of regulations brought in to reduce the impact that solvent-based coatings have on both worker health and the environment.
- One of the key challenges for water-based coatings is to significantly improve their anti-corrosion performance in line with solvent based systems. In doing so, this will fully extend the use of water-based systems to broader industrial protective coatings.



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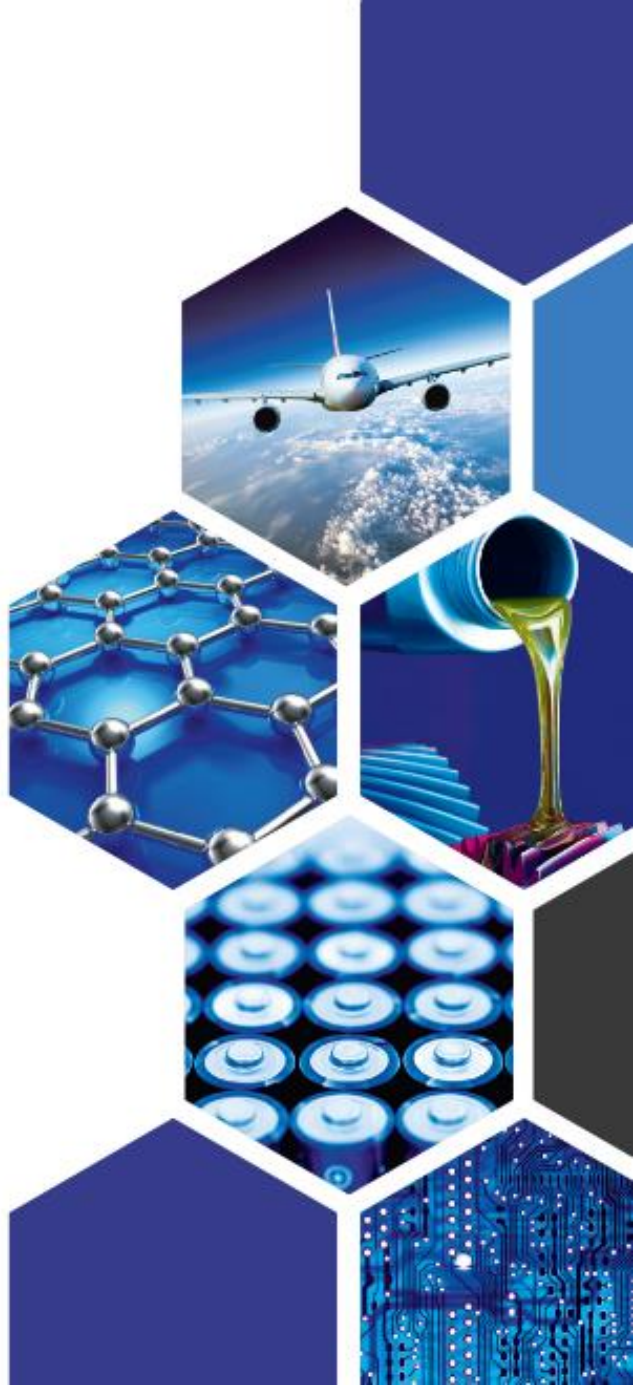
Genable® 1250 – Water Based Graphene Dispersion

AGM supplies its Graphene nanoplatelets in stable dispersions that are:

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

Genable® 1250 – AGM's Water-based Graphene Dispersion:

- **Milled to a controlled and optimised particle size to optimise barrier properties**
- **6 months shelf life**
- **0.5% Graphene loading by weight but has a Graphene volume solids of 51%**



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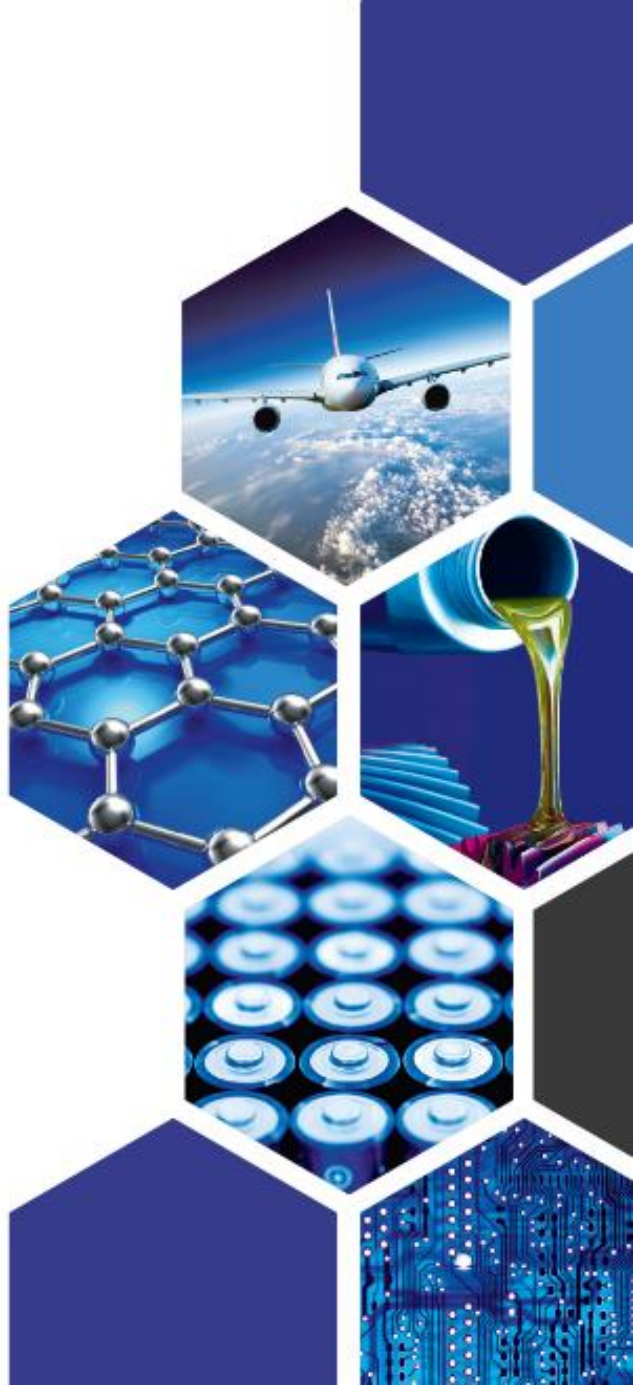
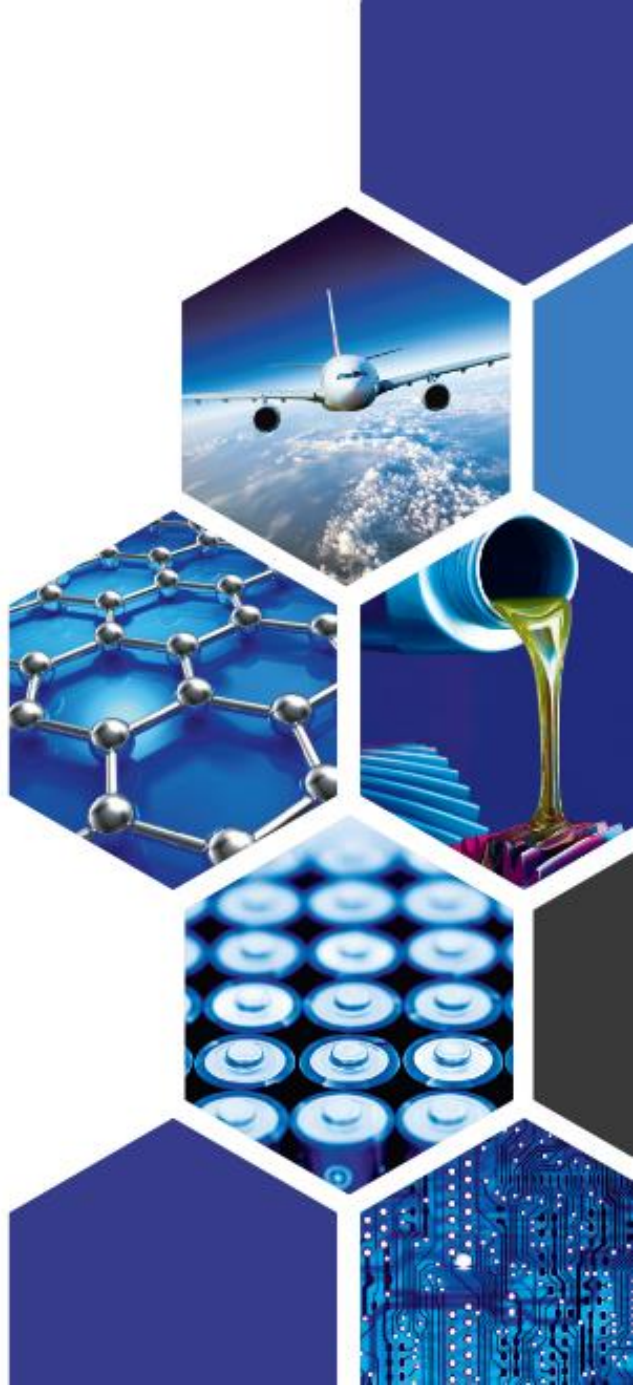
Experimental



Prototype Paint Formulation

Material	Control	Graphene DTM	Graphene Primer
Deionised Water	6.1%	6.6%	5.5%
Dispersant	1.8%	2.0%	1.6%
Defoamer	0.4%	0.5%	0.4%
Titanium Dioxide	26.0%	10.1%	23.4%
Rheology Modifier	1.7%	1.8%	1.5%
Alkyd Acrylic Resin	60.3%	65.1%	54.2%
Ammonia (29%)	0.4%	0.5%	0.4%
Combination Dryer	0.7%	0.7%	0.6%
Wetting Agent	0.3%	0.3%	0.3%
Flow Additive	0.5%	0.5%	0.5%
Anti-Skinning Additive	0.8%	0.9%	0.8%
Flash Rust Inhibitor	1.0%	1.0%	1.0%
Genable® 1250	-	10.0%	10.0%
Total	100%	100%	100%
Graphene Loading	***None***	***0.05%***	***0.05%***



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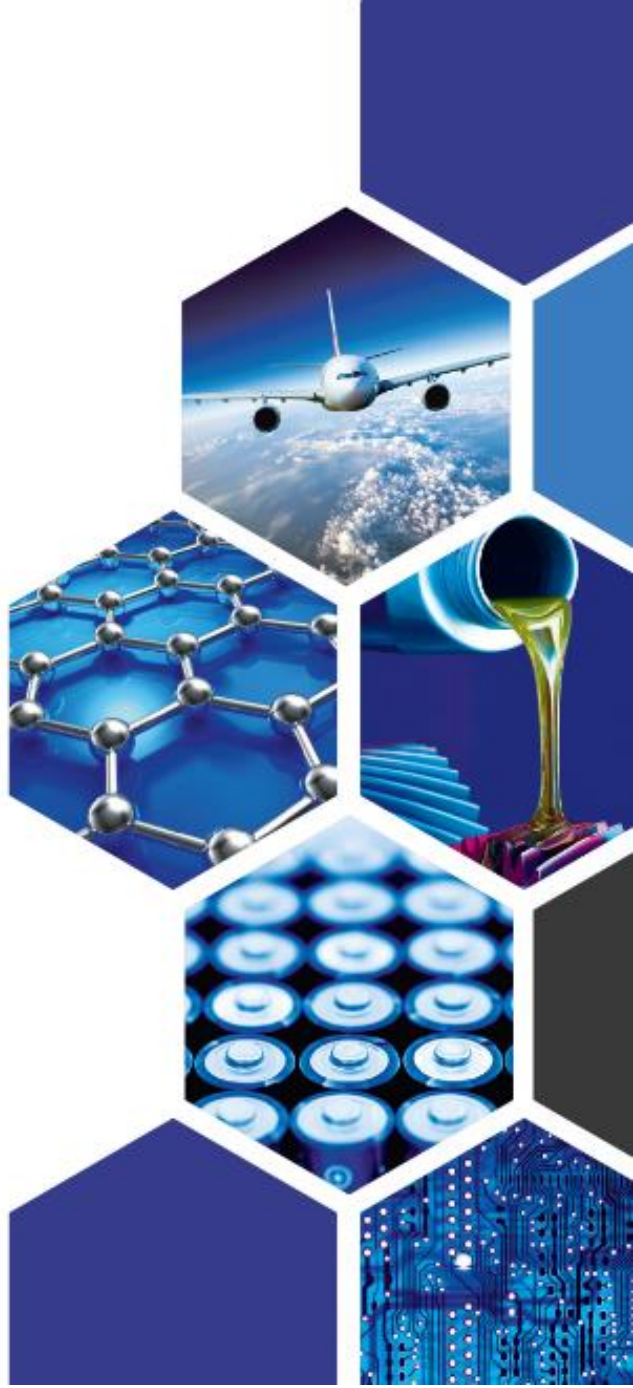
Work Programme – Part 1

Test Program I: Initial Scoping

- **Prototype primer formulations were developed based on an alkyd acrylic resin.**
- **Graphene nanoplatelets introduced with the addition AGM industry leading stabilised water-based GNP dispersion, G*enable*® 1250**
- **Coatings applied to abraded steel, blasted steel and iron phosphated steel**
- **Films were applied using drawdown bar at a wet film thickness of 150 microns**
- **Dry film thickness achieved for all systems was ~50 microns**
- **Dried under ambient lab conditions for 7 days**
- **Tested up to 1000 hours on Neutral Salt Spray**



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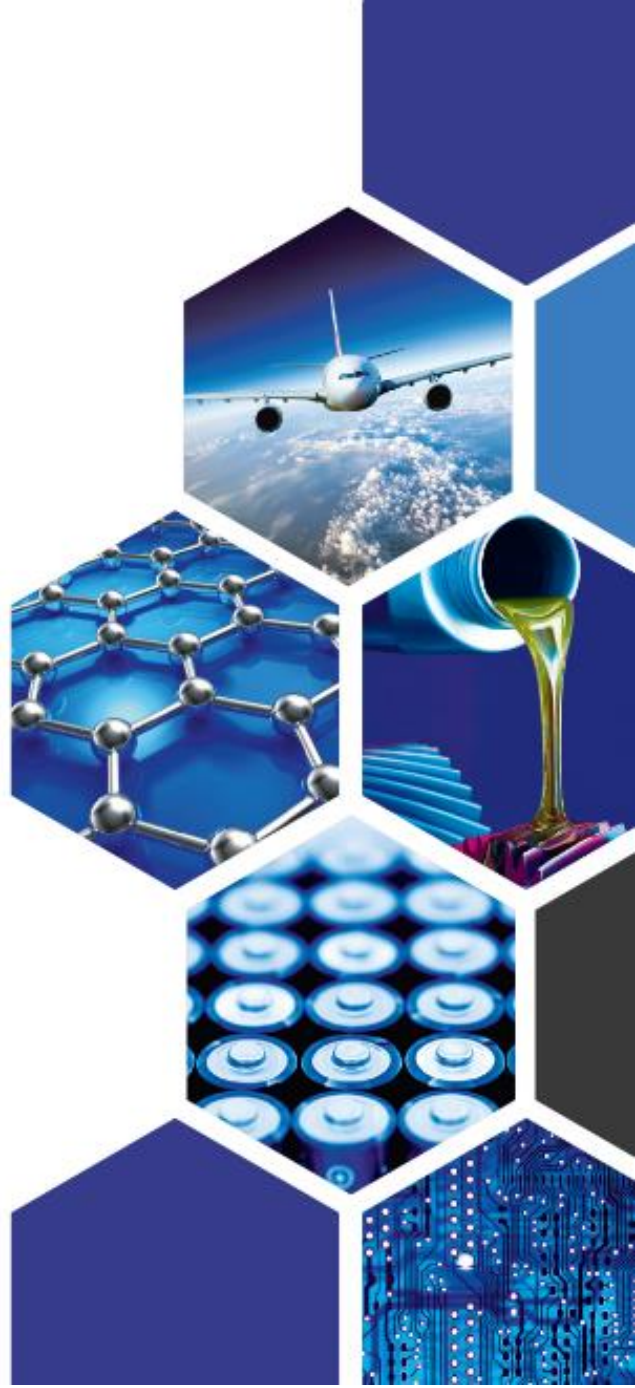
Neutral Salt Spray after 1000 hours – Creep Assessments

Neutral Salt Spray Testing using ISO 9227:

- **A ladder study of increasing G*enable*® 1250 loadings in a standard alkyd-acrylic primer system was tested against a blank control primer**
- **Formulations tested on three substrates – blasted steel, abraded steel and iron phosphated (Bonderite) steel**
- **Panels were visually assessed for creep, blistering and break-through corrosion after 1000 hours**



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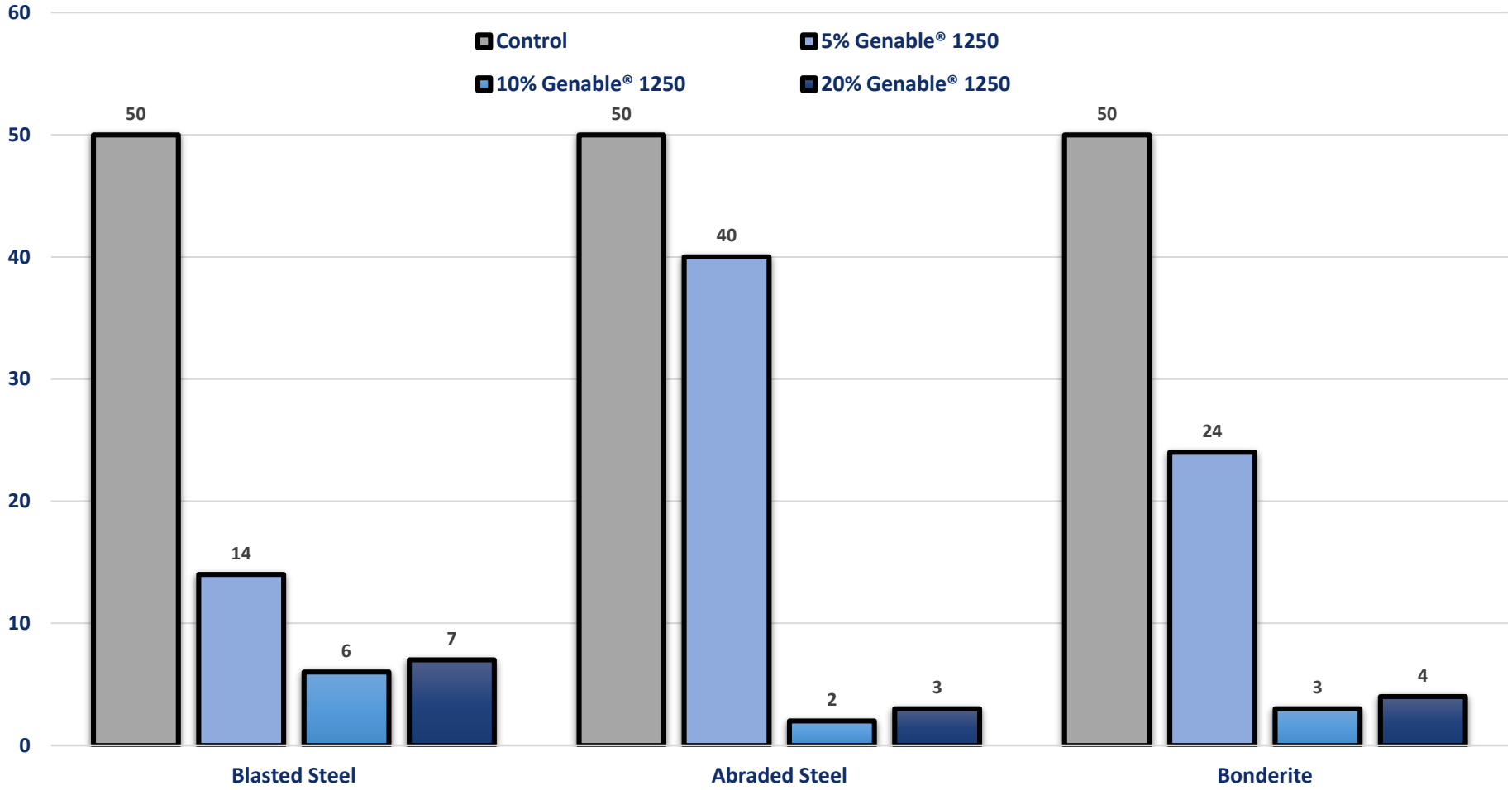
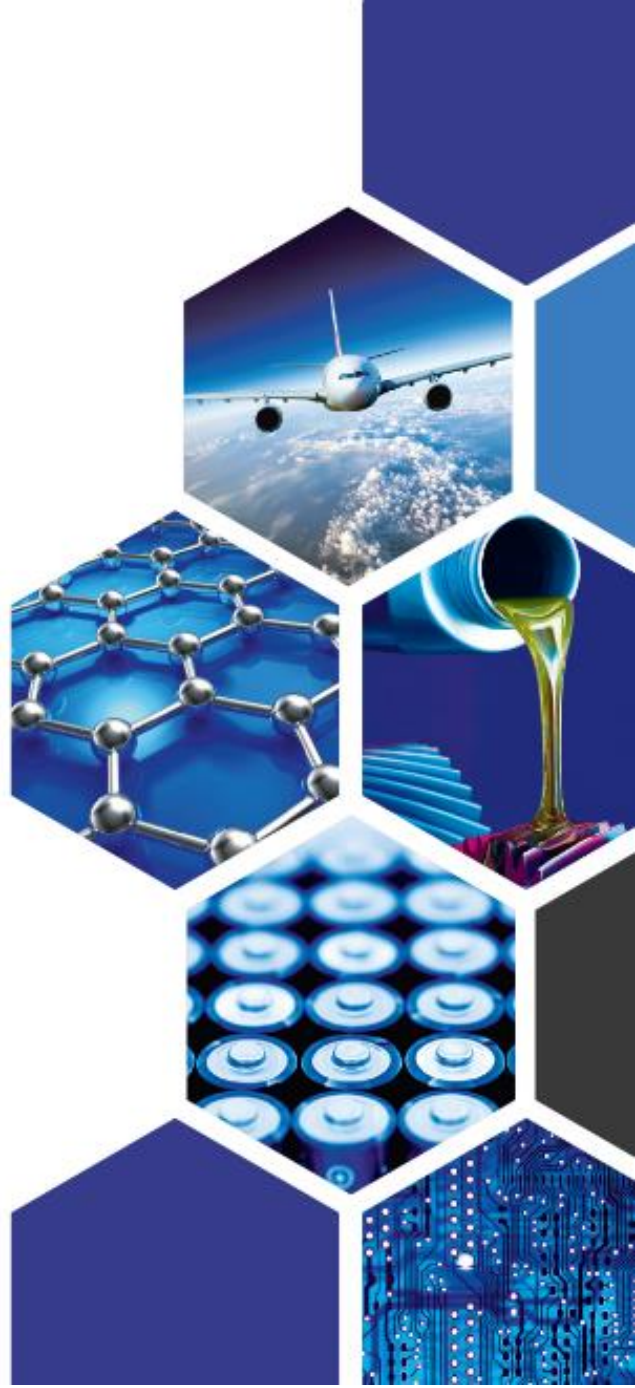
Neutral Salt Spray after 1000 hours

Average Creep (mm) across the Scribe of GNP Primer Ladder Study



- **With each loading of graphene, a significant reduction in the levels of creep was recorded compared to the control**



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Neutral Salt Spray – Visual Assessment

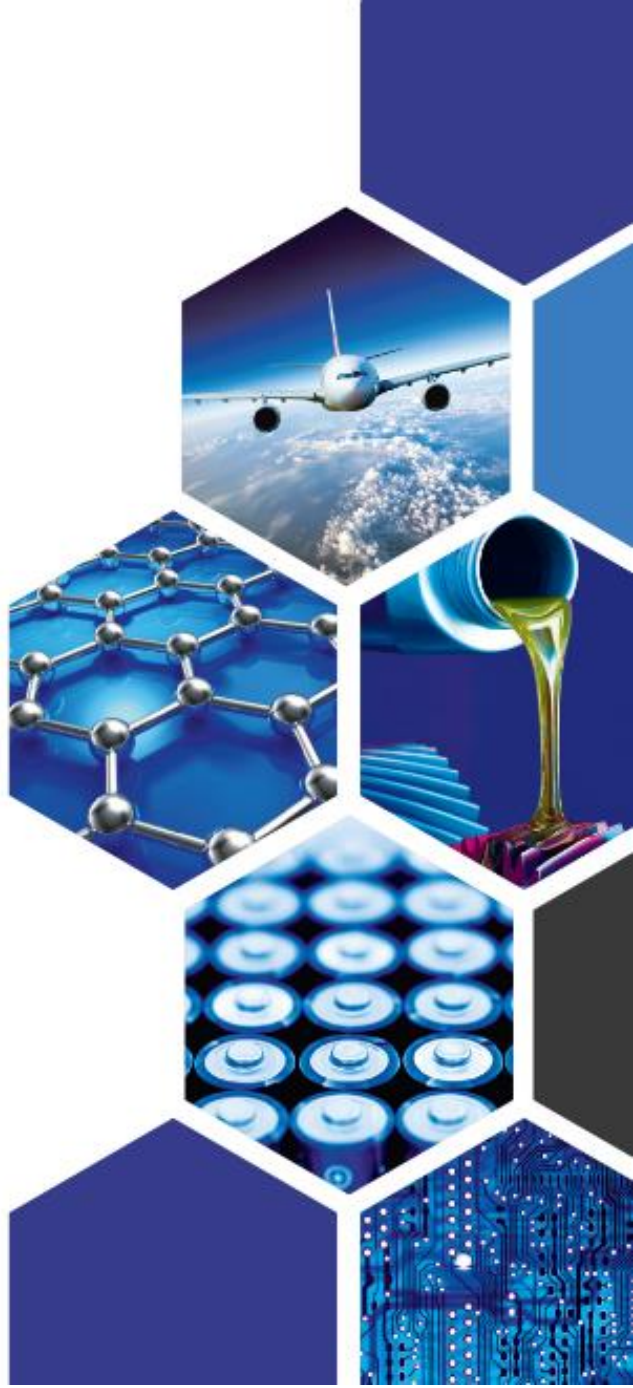
Abraded Steel

Control (No GNP)

PVC: 20

10% G*enable*® 1250

PVC: 30



Test Programme – Part 2

Further development of graphene enhanced Direct-To-Metal and Primer formulations

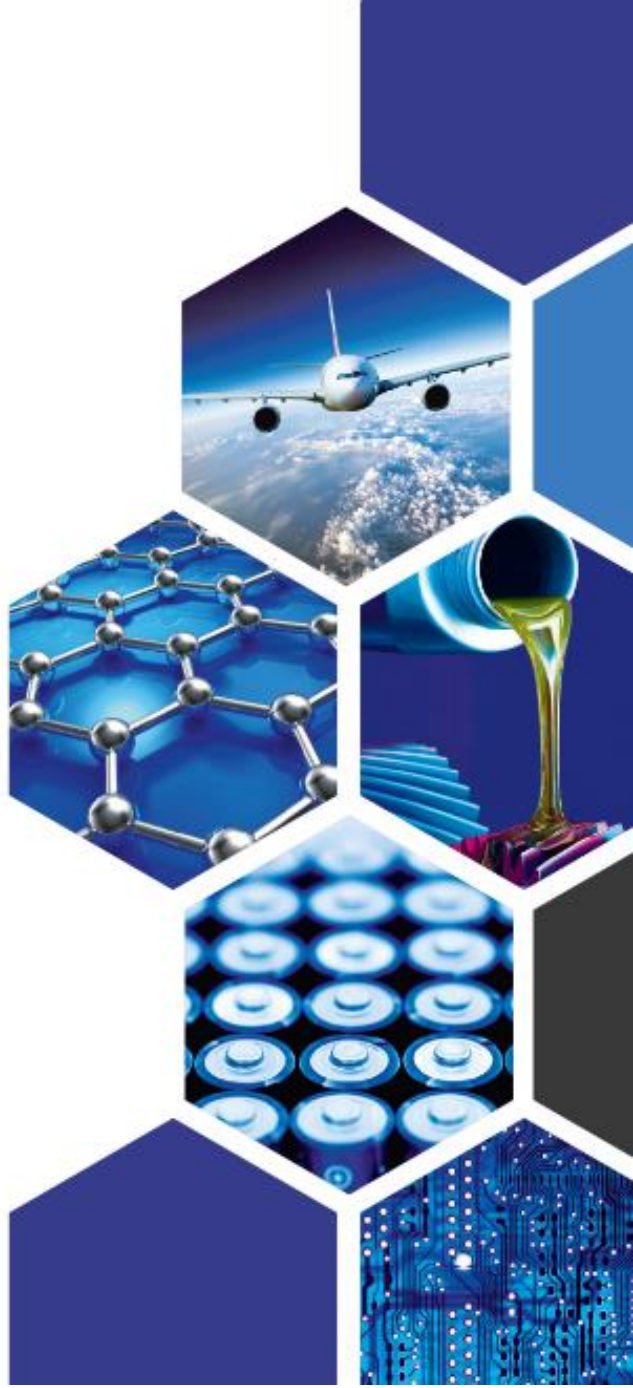
- Viscosity
- Colour
- Gloss

Electrochemical Studies

- Impedance
- Water Uptake

Systems tested:

- Graphene enhanced Direct to Metal formulation
- Graphene enhanced waterbased primer



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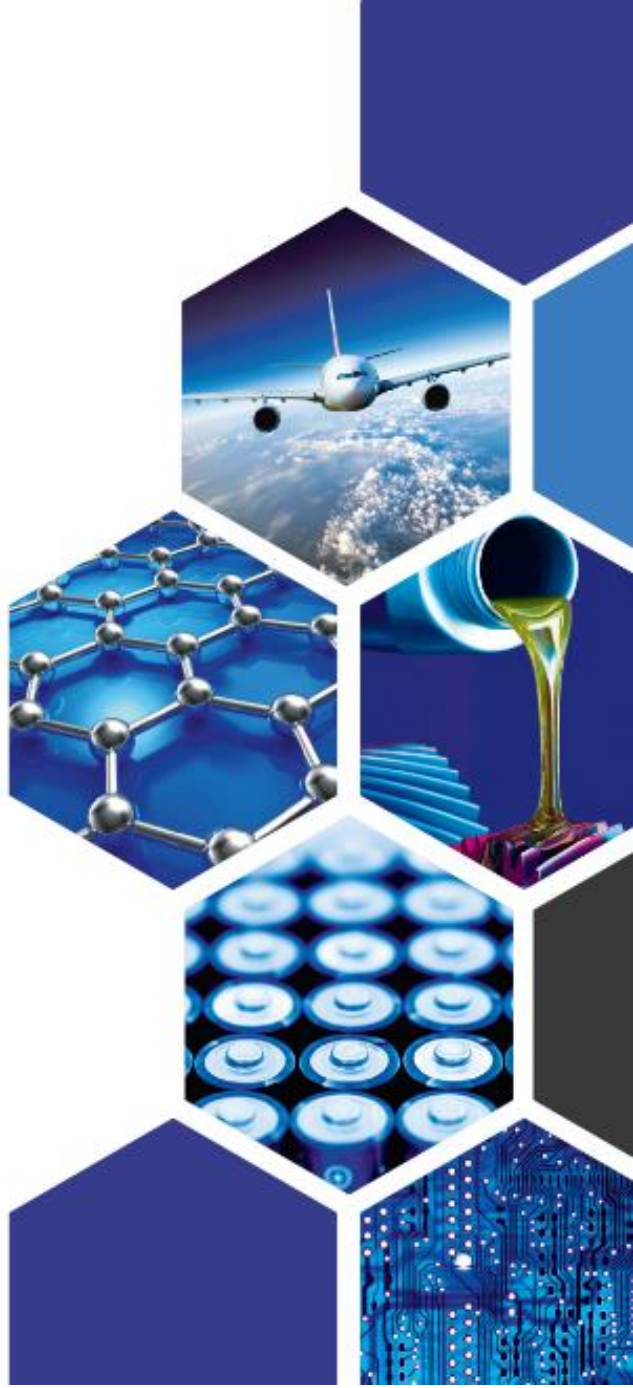
Effects on Colour and Gloss from GNP

System	PVC	VOC (g/l)	Viscosity (Pa.S)	60° Gloss	L*	a*	b*
Control White Primer	20	10.4	14.6	84.1	96.8	-1.3	4.9
DTM Graphene Paint (grey)	20	11.3	1.8	85.3	68.8	-1.0	-0.8
Graphene Primer (grey)	30	9.4	4.3	80.2	77.1	-1.3	-1.7
Commercial Grey primer	*No data*	*No data*	*No data*	6.4	50.8	-0.8	-1.3

- **Graphene addition has minimal impact on the gloss of the paint**
- **Graphene acts as an excellent black pigment, giving a primer with a light grey hue**
- **The Graphene paints, in comparison with a commercially available grey primer, were still lighter in shade allowing scope for further colour matching.**
- **The addition of the high surface area graphene, due to its easy to use dispersed form does not impact on the viscosity of the finished paint**



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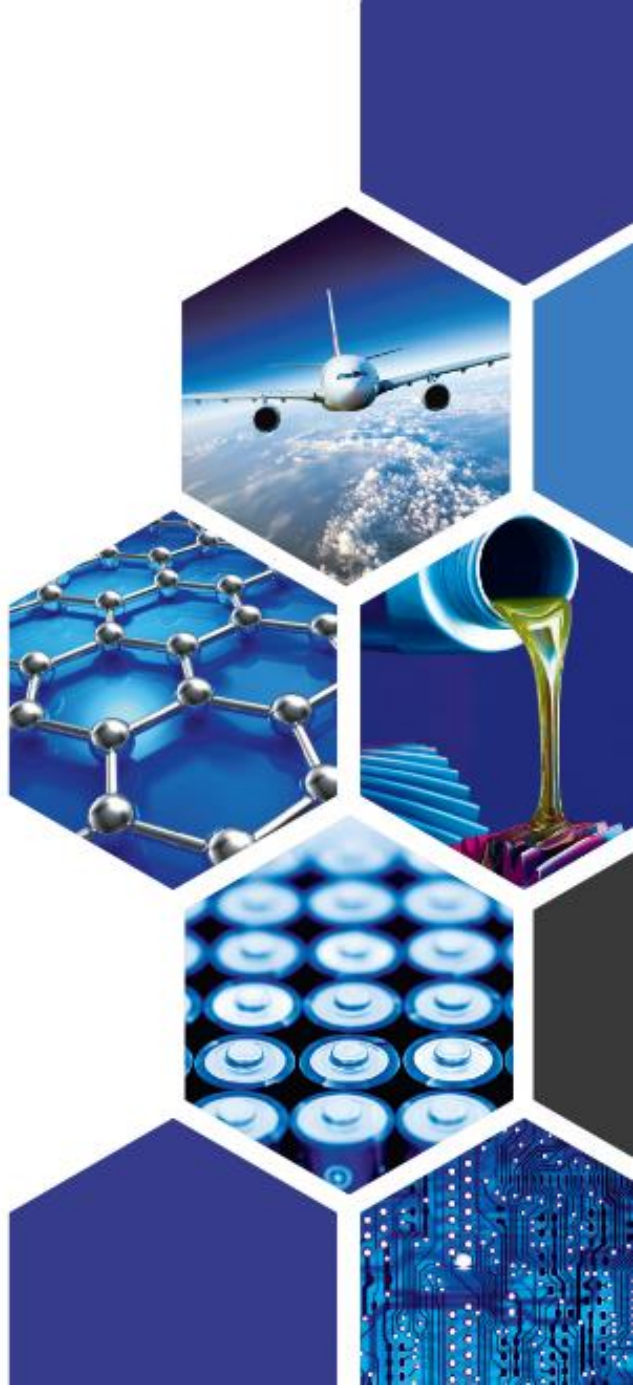
Electrochemical Studies



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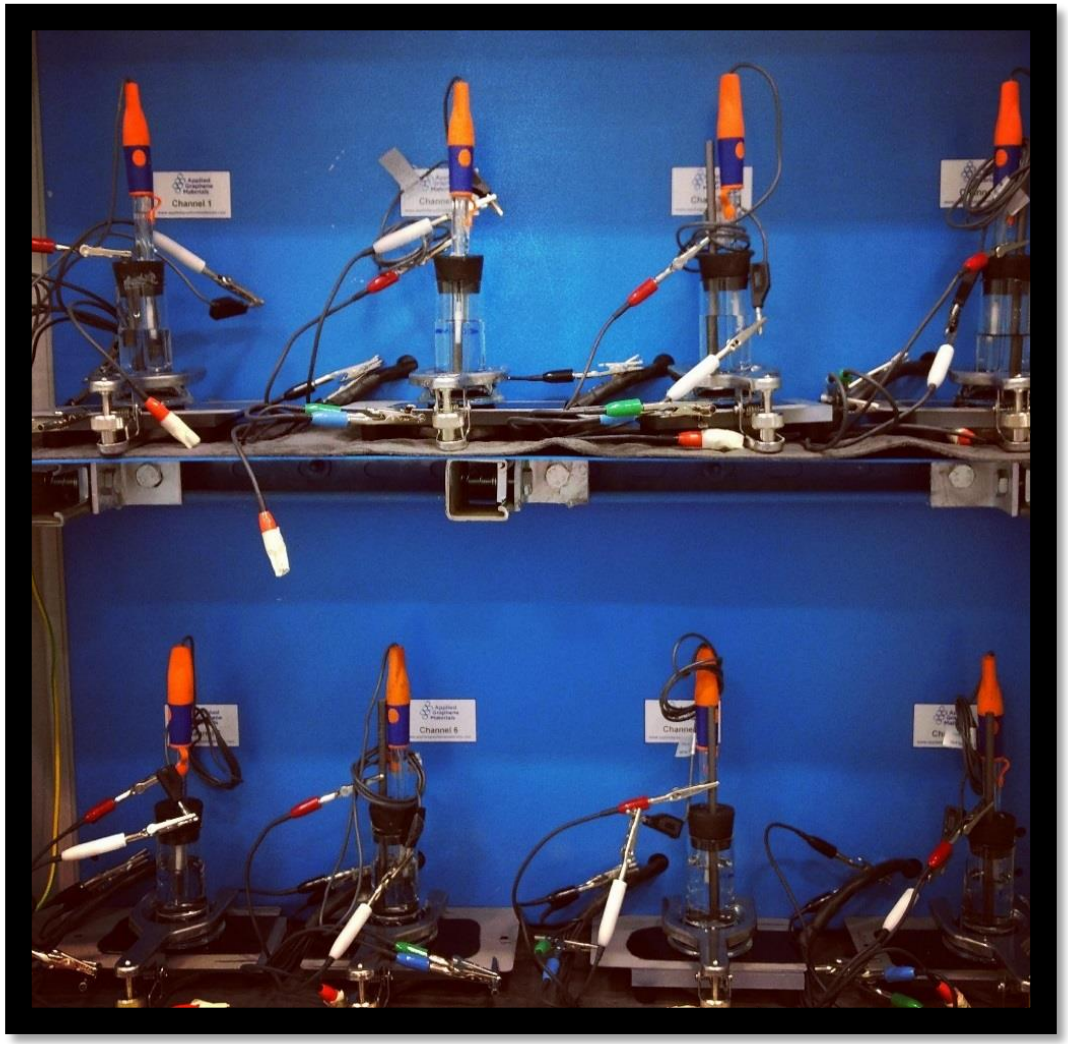
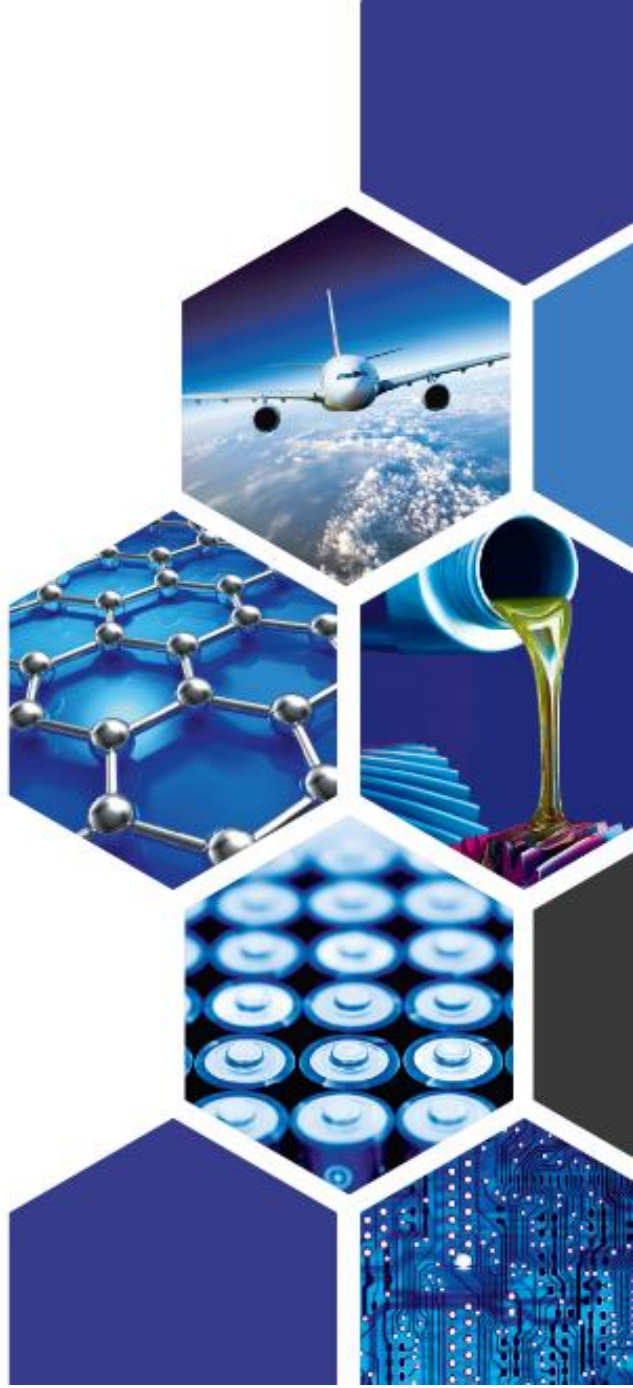
Electrochemical Impedance Spectroscopy Testing



- Measurements recorded using a Gamry 1000E potentiostat with a Gamry ECM8 multiplexer
- Working electrode test area = 14.6 cm^2
- 3.5wt% NaCl electrolyte
- Continuous measurements taken over a 140 hour period.



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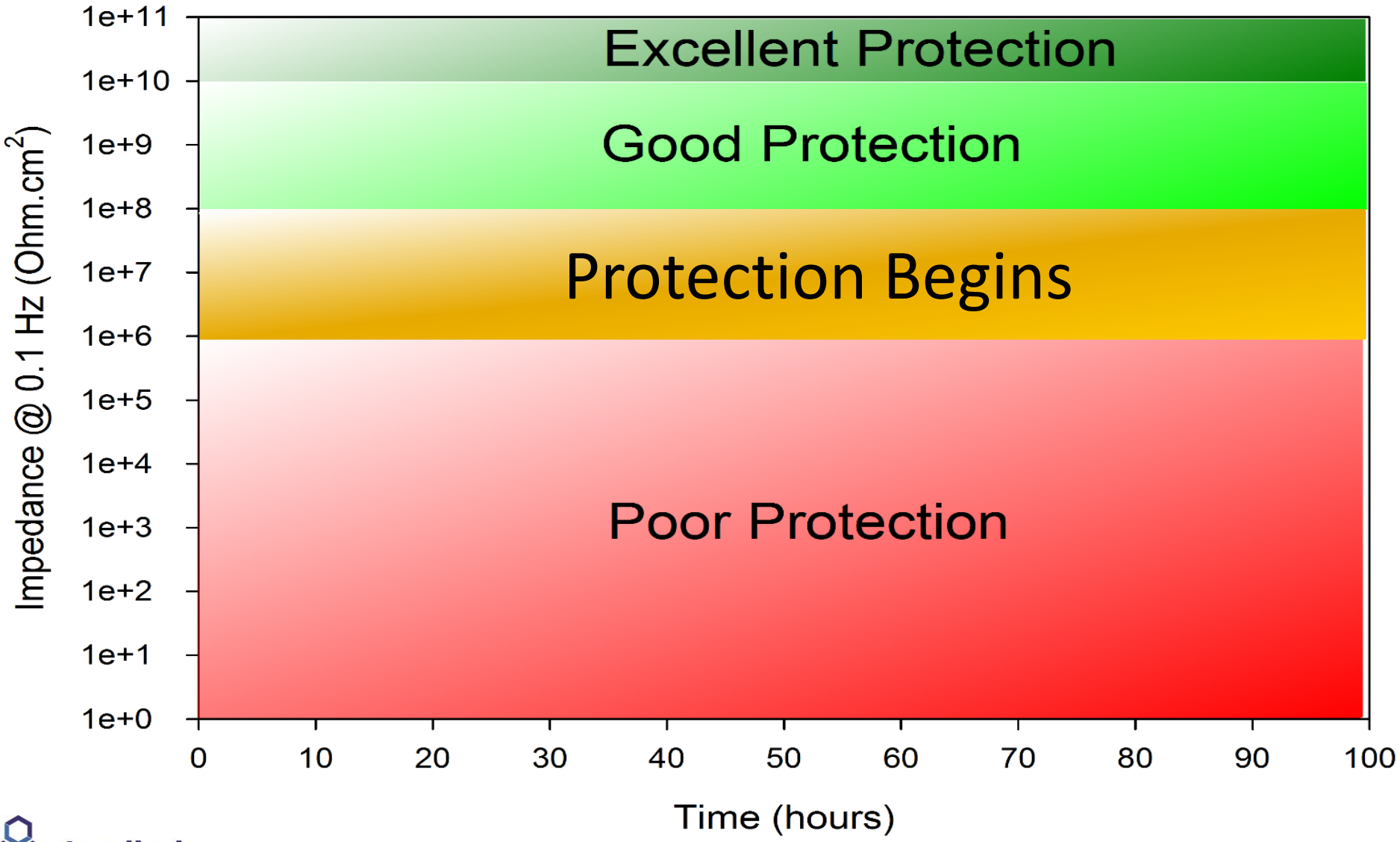
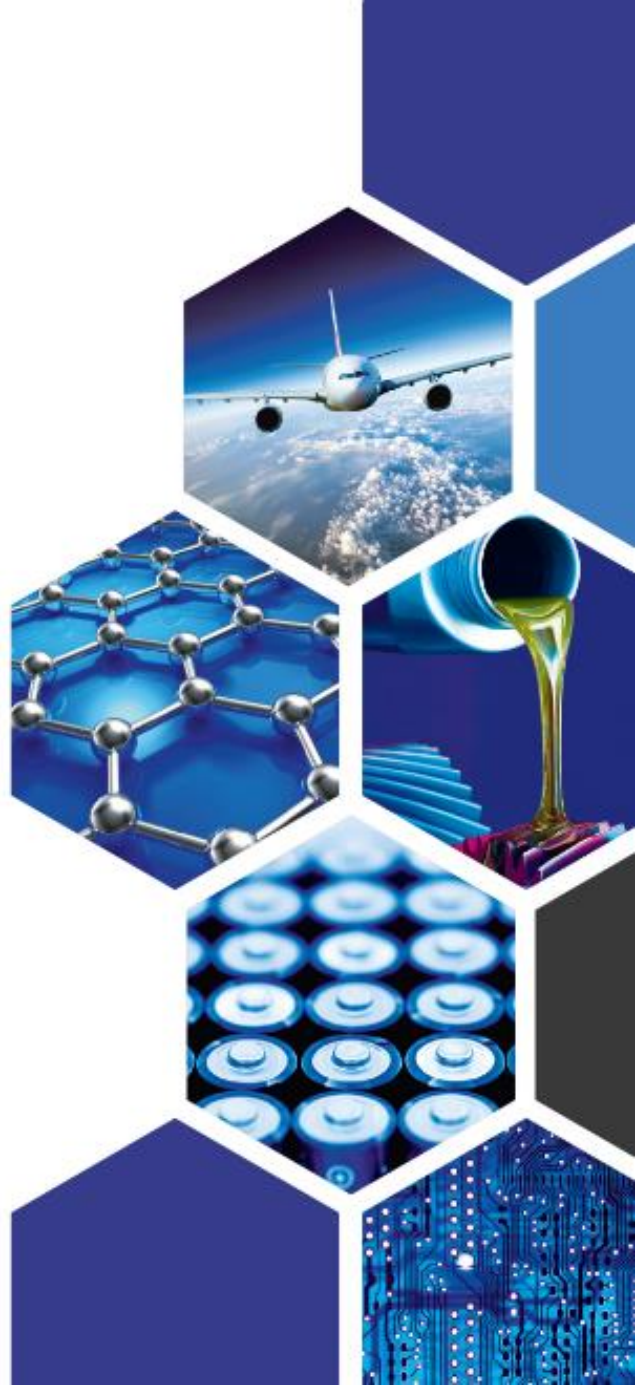
AC Impedance (EIS) – Zones of Protection





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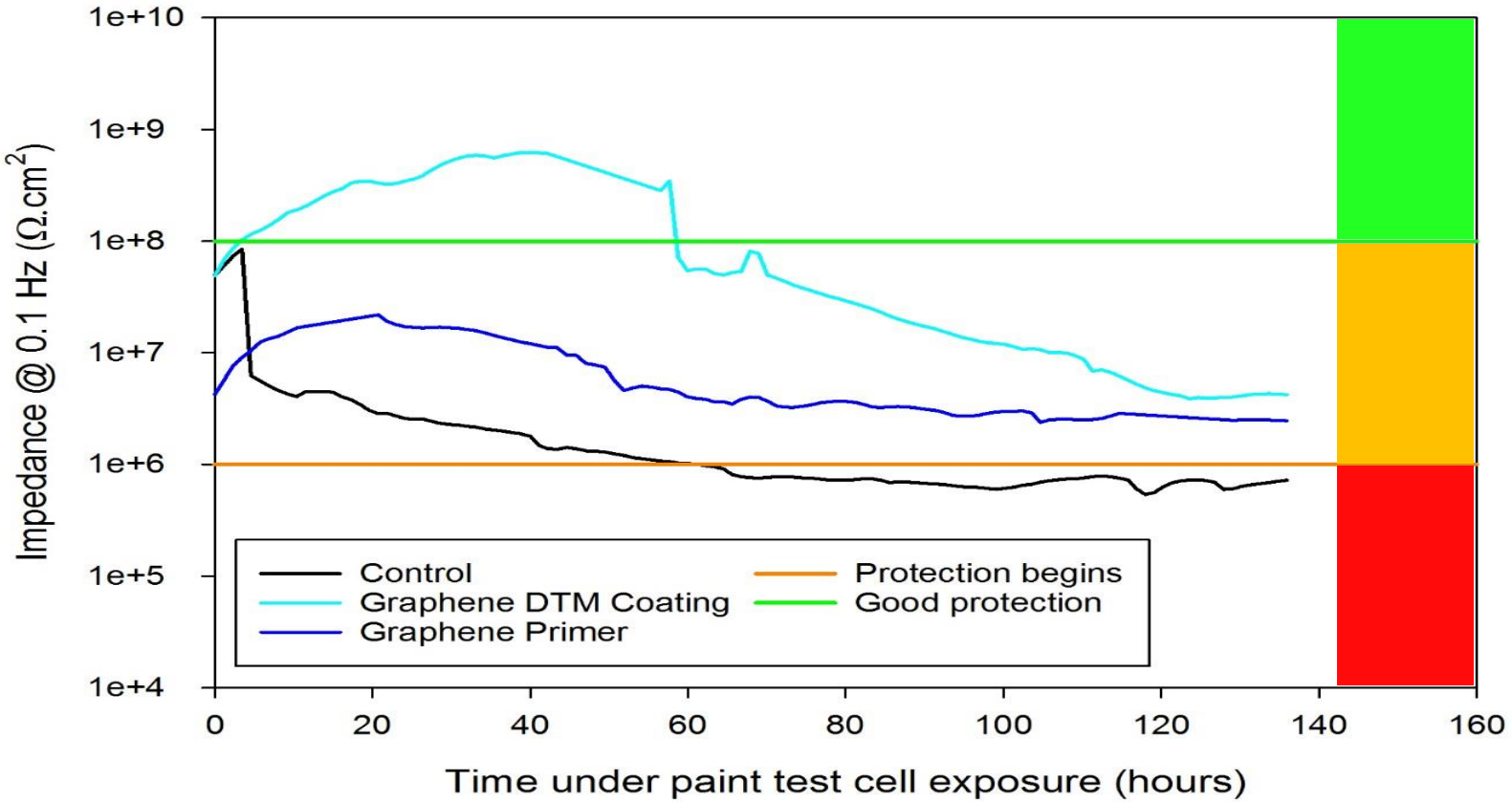
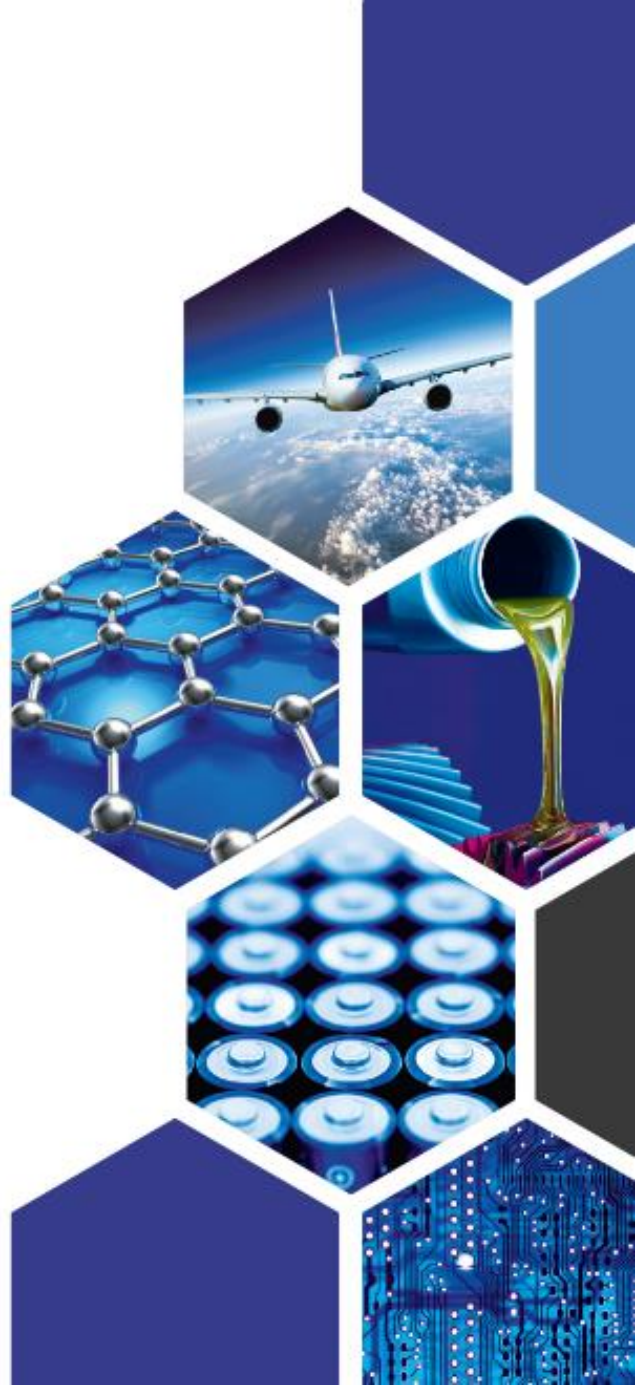
Effects on Colour and Gloss from GNP



- **The graphene enhanced primer and DTM coatings showed higher impedance values than the graphene-free control.**
- **Higher level of impedance was achieved with the DTM coating due to PVC.**



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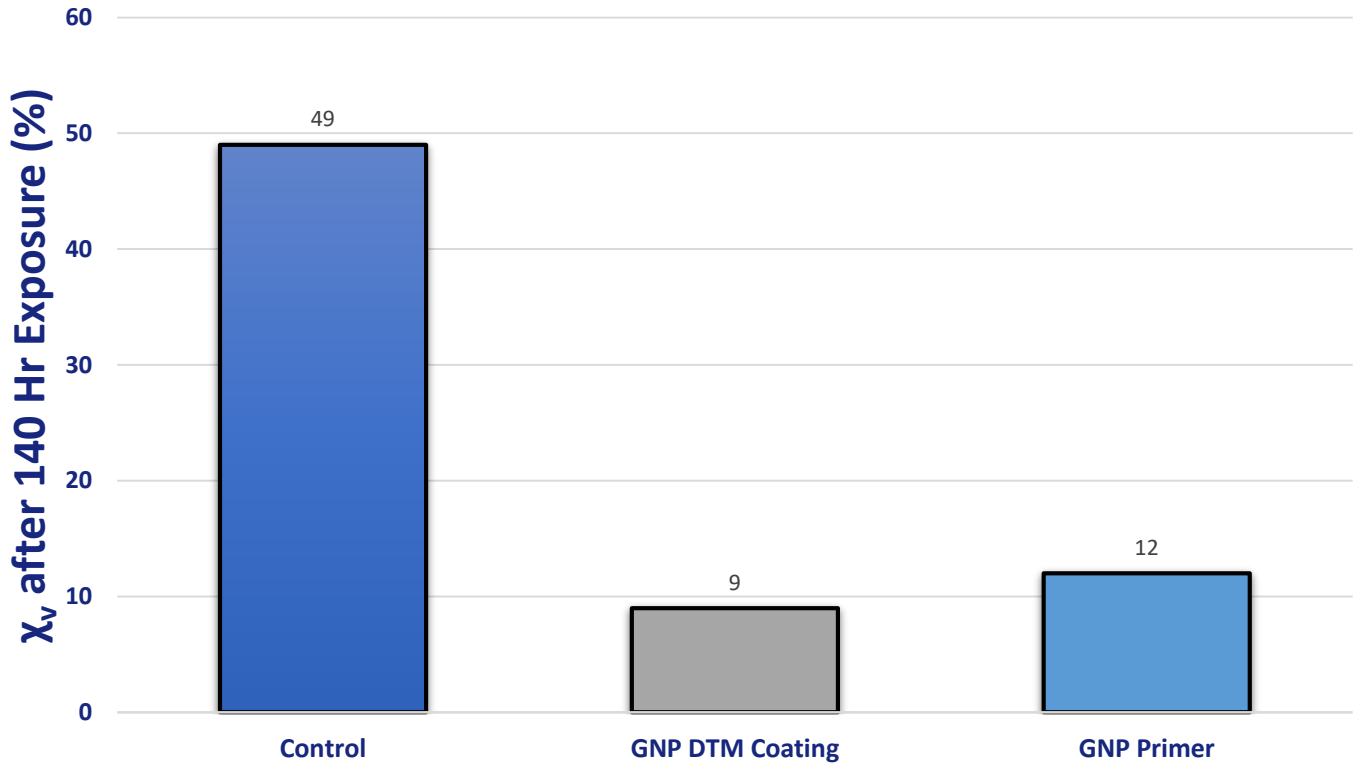
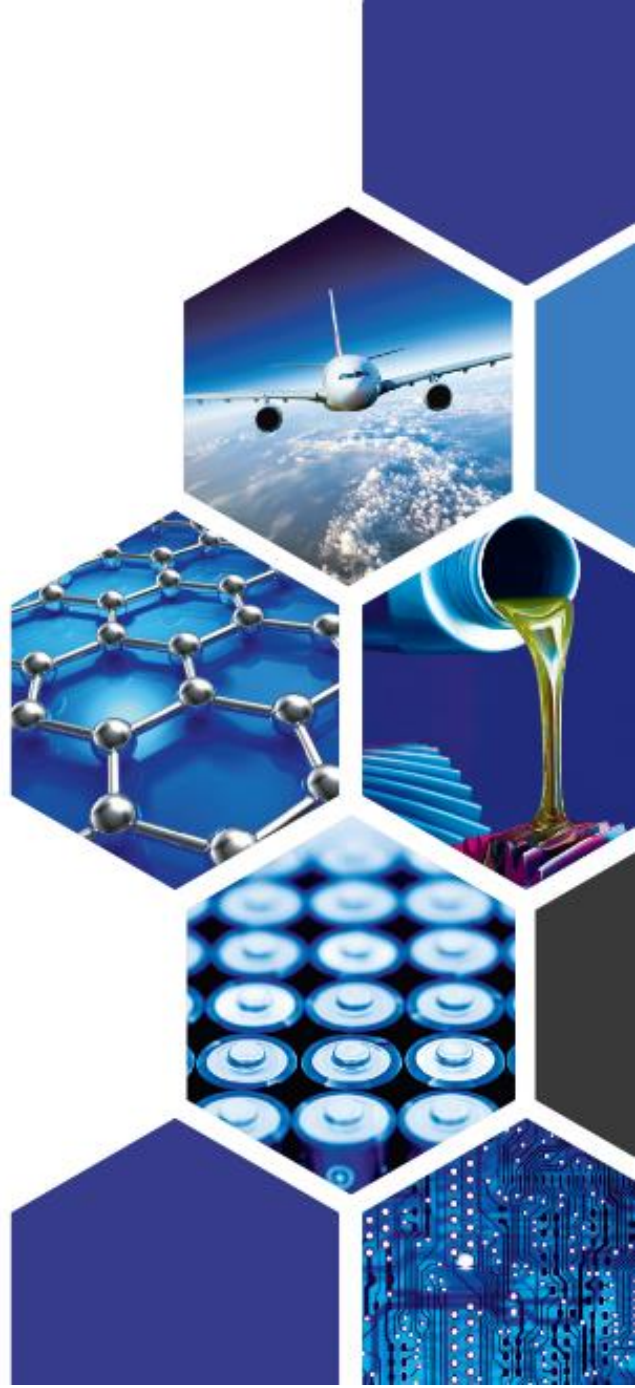
Water Uptake



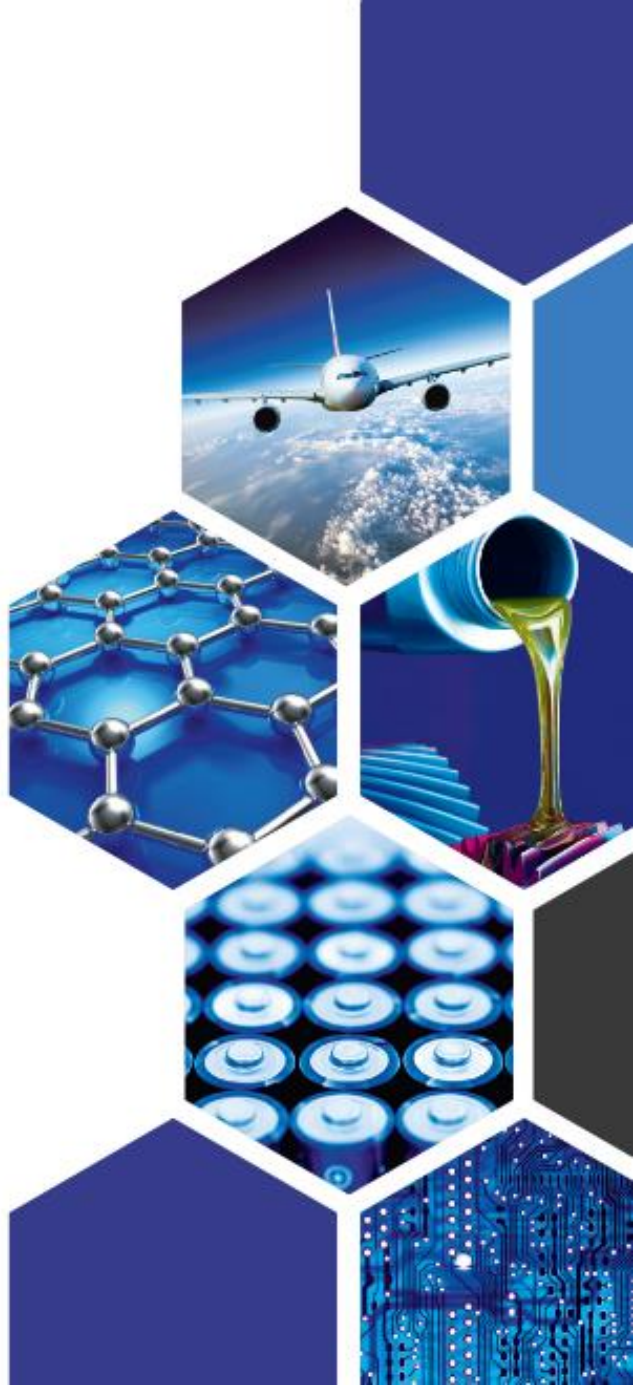
- **The addition of 10% G*enable*® 1250 resulted in a significant reduction in water uptake.**
- **Both systems showed a 35-40% reduction**
- **The reduction in water uptake suggests the graphene nanoplatelets are improving barrier properties by increasing the tortuous path.**



Summary

The test results presented here clearly demonstrated performance gains in waterbased anticorrosive systems:

- **Significant reduction in creep**
- **Reduction in visible corrosion on 3 types of steel tested**
- **Greater than 35% Reduction in water uptake with the addition of 10% G*enable*® 1250 in both the DTM and primer formulations.**
- **Higher impedance values with the graphene coatings compared to the control demonstrating a significant increase in barrier performance**



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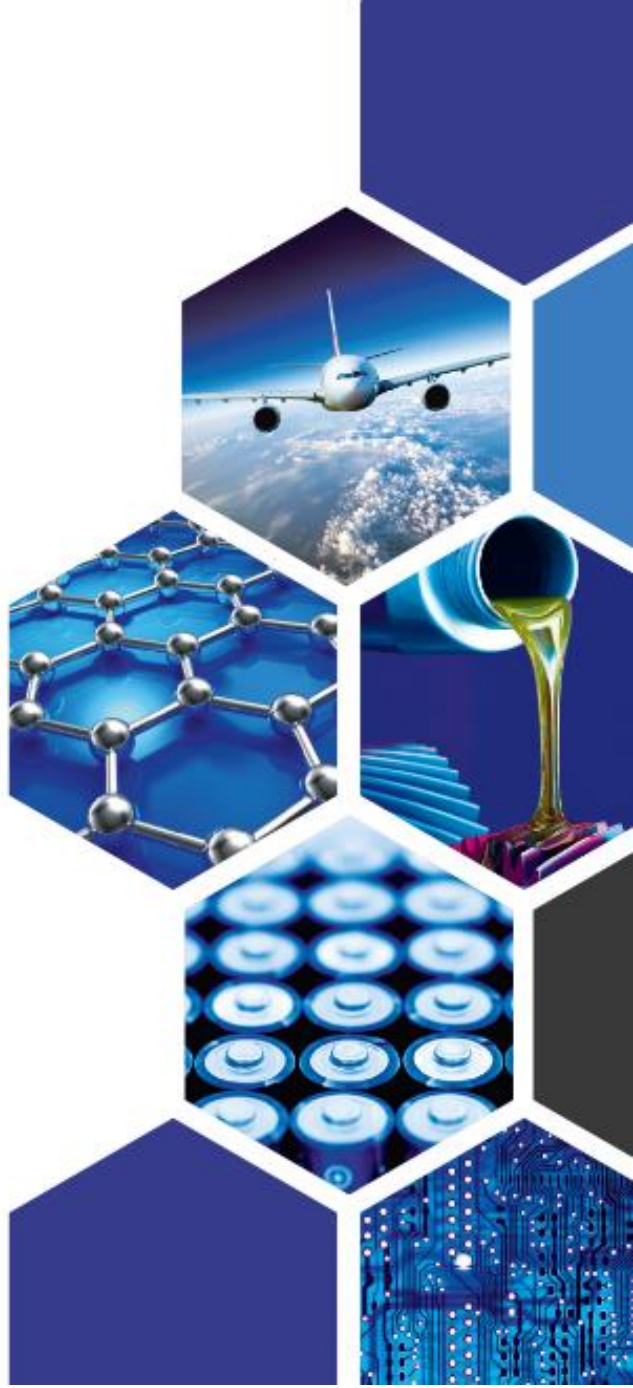
Conclusion

- AGM has developed a range of prototype water-based coatings containing graphene nanoplatelets.
- With minimal impact to coating gloss and a slight drop in L* values, the resultant grey coatings were lighter than the commercial grey primer testing allowing formulators significant room to colour match.
- With the addition of Graphene nanoplatelets delivers a significant increase in corrosion resistance as well as a reduced creep and water vapour uptake.
- Through adding the high surface area and high aspect ratio graphene nanoplatelets, AGM are able to offer formulators a new toolbox of technology to drive the innovation of water-based anti corrosion coatings.



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