



APPLIED GRAPHENE MATERIALS

TECHNICAL APPLICATION NOTE

Waterborne Coatings: Waterborne Epoxy Coatings

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1. Introduction

Applied Graphene Materials UK Ltd (AGM) manufacture graphene nanoplatelets (GNPs) using a proprietary and patented process developed at Durham University in the UK.

AGM have developed significant in-house knowledge on the behaviour and performance of graphene modified coating formulations. These guidance notes are designed to provide formulation insights to assist development scientists achieve a technical appreciation of this novel technology.

The addition of graphene alone by a **Genable**[®] dispersion into coating formulations has demonstrated excellent barrier properties leading to a reduction in water-vapour transmission rates (WVTR). This reduction in WVTR significantly enhances the anti-corrosive performance of an epoxy coating. (This improvement is discussed in more detail in AGM's Technical Guidance note on Anti-Corrosion Primers: Part 1).

1.1. Waterborne Epoxy Coating

Waterborne technology has seen growth with an increasing interest in sustainability, observable through stricter environmental regulations and growing end user demand for environmentally friendly technology. Despite the advances in waterborne solutions high-corrosion-resistant coatings remain largely solvent borne because of manufacturers' needs for high chemical and weather resistance that cannot yet be achieved with water-based coatings. Nevertheless waterborne DTM system find utility in interior spaces where condensation may be an issue or in exterior environments with low levels of pollution such as tanks, steel doors, rail cars. Waterborne epoxy primers in conjunction with PU top-coats are utilised in C2-3 type environments ISO12944-2 and ISO9223. Waterborne epoxy primer systems may be used on C2.05 medium risk environments for hidden steelwork or visible steelwork. This technical application note (TAN) describes in further detail how the addition of **Genable**[®] dispersions to waterborne epoxy systems may be utilised to improve corrosion performance.

2. Anti-Corrosion Evaluation

The objective of the work in this technical note was to evaluate and determine if graphene nanoplatelets can enhance the performance of the corrosion protection in coating systems to deliver a meaningful extension of life to a C2-C3 category coating according to ISO 12944.

Testing Carried Out

Accelerated Testing:	Salt Spray Testing	ASTM G-85-94 Prohesion
	Salt Spray Testing	ISO 9227 Neutral Salt Spray
	Corrosion Creep Assessments	ISO 4628-8
Mechanical Testing:	Flexibility	ISO6860:
	Impact	ISO6272-2:2004
	Adhesion	ISO 4624

2.1. Typical Graphene-Based Waterborne Epoxy Formulation

The evaluation was conducted using the control and graphene-modified waterborne epoxy formulations (**Table 1**) below:

Part A: Epoxy Base				
Item	Raw Material	Weight%		
		Control	5% Genable® 1250 System	10% Genable® 1250 System
1	Beckopox EP 2384w/57wa	34.45%	36.35%	38.02%
2	Additol VXW 6208	1.34%	1.41%	1.48%
3	Additol VXW 6393	0.26%	0.27%	0.28%
4	Luzenac 2310	4.81%	5.07%	5.31%
5	Kronos 2310	16.91%	12.14%	7.62%
6	Bayferrox 3920	0.21%	0.15%	0.10%
7	Bayferrox 318M	0.69%	0.49%	0.31%
8	Bartex 65	13.22%	9.49%	5.96%
9	Water	11.85%	12.51%	13.08%
10	Additol VXW 6388	0.60%	0.63%	0.66%
11	Genable® 1250 Dispersion	0.00%	5.00%	10.00%
12	HaloX Flash-X 150	1.00%	1.00%	1.00%
Part B: Curing Agent				
13	Beckopox VEH 2188w/55WA	13.12%	13.85%	14.48%
14	Water	1.54%	1.64%	1.70%
Total =		100.00%	100.00%	100.00%
Note: Weight% are based on the full system loading, Part A + Part B				
PVC		31.47%	31.47%	31.48%
Graphene Loading (AGNP-35)		0.00%	0.025%	0.05%

Table 1 – Formulation Weight%, PVC and Graphene Loading

2.2. Manufacturing Guidelines for Waterborne Epoxy Coating with Graphene Additive

It is recommended that **Genable®** dispersions should be added at the let-down stage of the manufacturing process.

Impact on PVC: For guidance please contact Business Development on the included contact details.

2.3. Test Panel Preparation

Substrate	Cold Rolled Steel
Dimensions	152 mm by 101 mm
Preparation	Grit blasting to SA2-1/2, acetone degreases
Grit	Irregularly shaped chrome/nickel shot
Application	Steel Drawdown Bar (300 µm)
Coating Thickness	DFT 80 – 100 µm
Curing	7 Days at Room Temperature (25 °C)

3. Extended Environmental Testing (ASTM G-85-94 and ASTM ISO 9227) Results

3.1. ASTM G85-94 Prohesion

When comparing the corrosion creep results shown in **Figure 1**, the 20% **Genable®** dispersion system shows the greatest improvement in corrosion resistance under ASTM G-85-94 Prohesion conditions. Addition of **Genable® 1250** dispersion to a 10% loading level shows a reduction of 43.1% in average corrosion creep recorded when compared to the control system at 2000 hours of exposure.

Likewise, in **Figure 2** the average corrosion is plotted over the exposure time to show the average rate of corrosion of the samples. Both graphene variant systems show a reduced rate of corrosion compared to the control system.

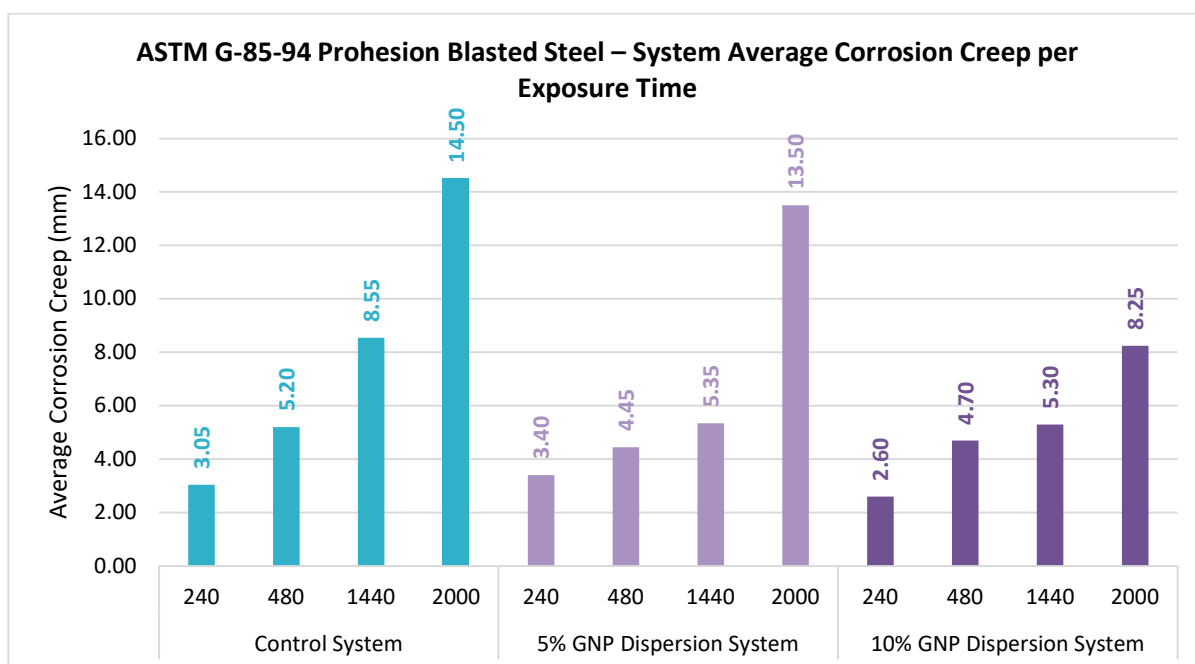


Figure 1 – ASTM G-85-94 Prohesion – System Average Corrosion Creep per Exposure Time

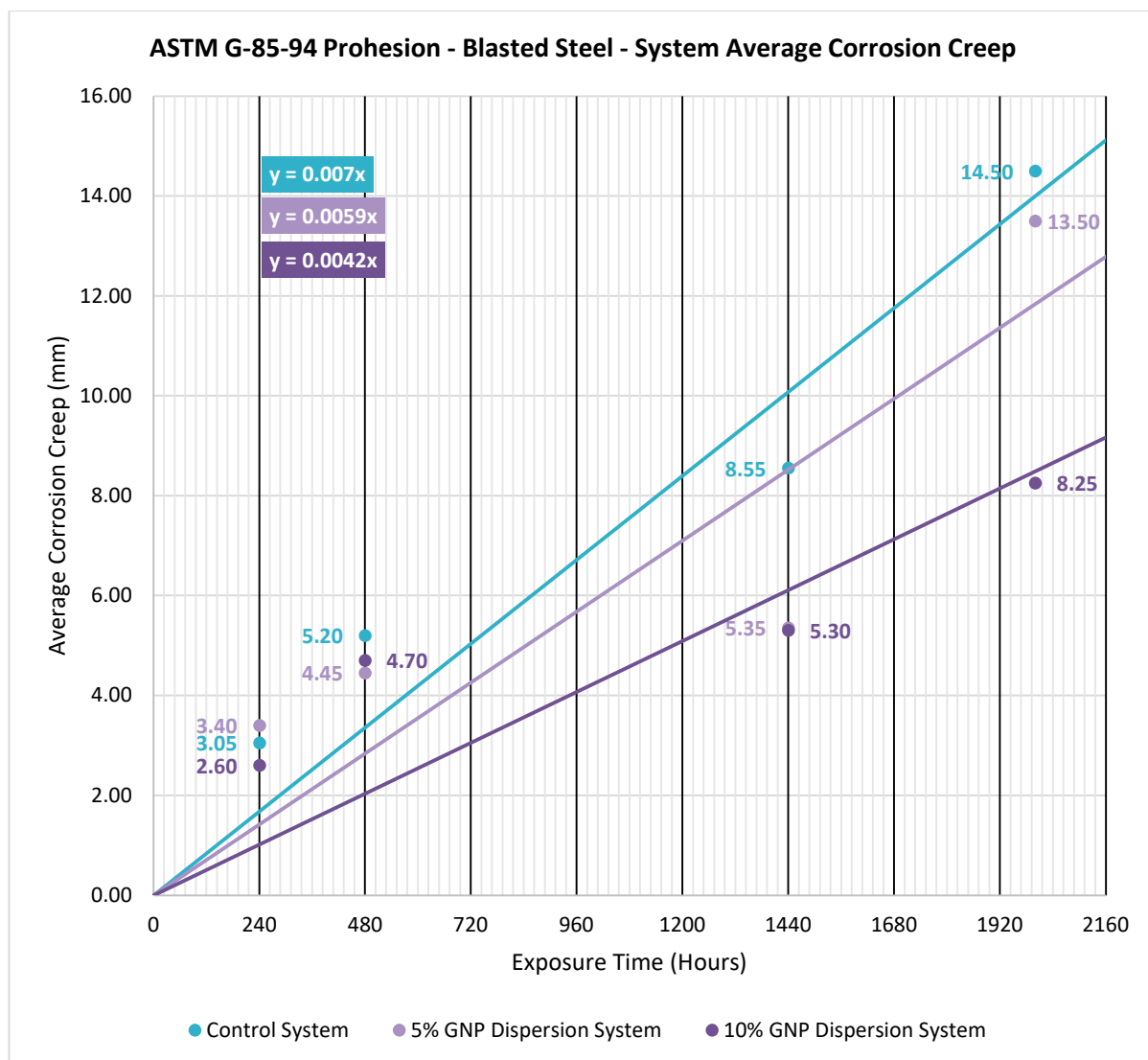


Figure 2 – ASTM G-85-94 Prohesion – Average Corrosion Creep vs. Exposure Time

System	Blister Rating						Location
	Micro	Size 1	Size 2	Size 3	Size 4	Size 5	
Control System	0	0	1.5	0.5	0	2	Around scribe
							Around scribe
5% GNP Dispersion System	0	0	1	2.5	0	1	Around scribe
							Around scribe
10% GNP Dispersion System	0	0	3	0	0	0	Around scribe
							Around scribe

Table 2 – ASTM G-85-94 Prohesion (2000 Hours) Blistering Results

Blistering (**Table 2**) occurred mainly around the scribe, rather than in the bulk of the coating. This infers that little water penetration has occurred in these bulk sections, or that little ionic salts have penetrated through which would normally result in blistering. The blistering around the scribe observed is likely due to the undercutting and creep of corrosion from the intentional defect. There is

little consistency in the blistering observed up between the samples evaluated at different exposure time intervals.

3.2. ISO 9227 Neutral Salt Spray

When comparing the corrosion creep results shown in **Figure 3**, both the tested **Genable® 1250** systems show an improvement in corrosion resistance when compared to the control variant. The systems, a 5% and 10% loading of **Genable® 1250** dispersion show a reduction in average corrosion creep of 30.0% and 36.5% respectively at 2000 hours of exposure.

In **Figure 4**, the average corrosion is plotted over the exposure time to show the average rate of corrosion for the systems. Again, the **Genable® 1250** systems show a lower average rate of corrosion when compared to the control system over the course of 2000 hours of exposure.

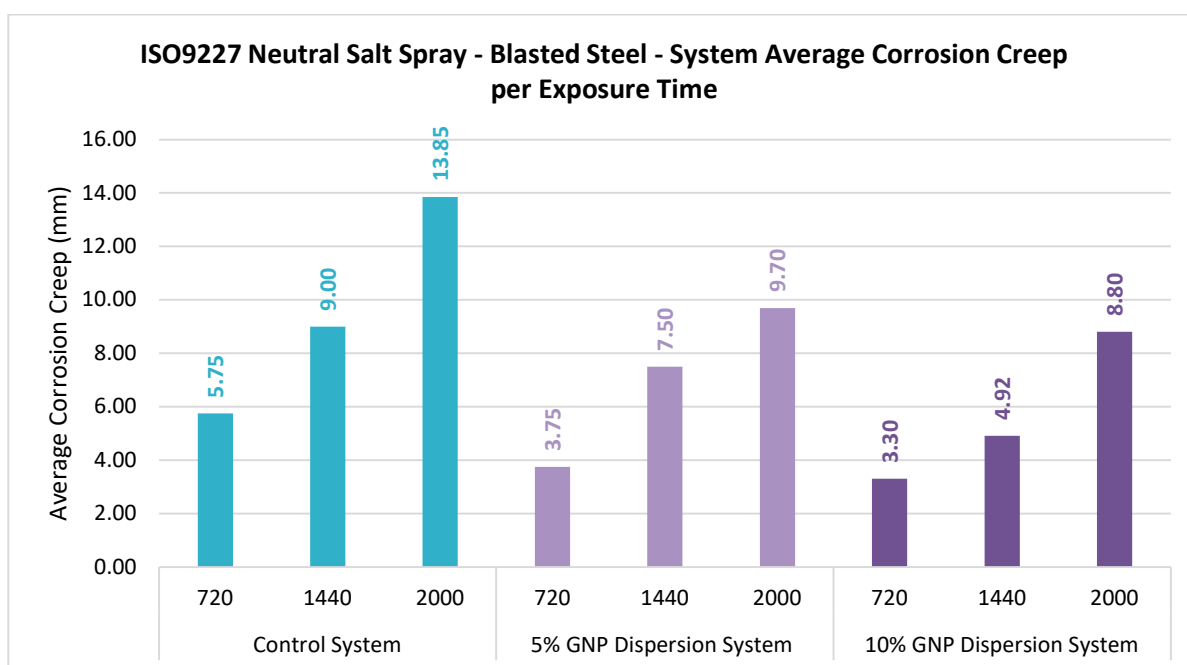


Figure 3 – ISO9227 Neutral Salt Spray – System Average Corrosion Creep per Exposure Time

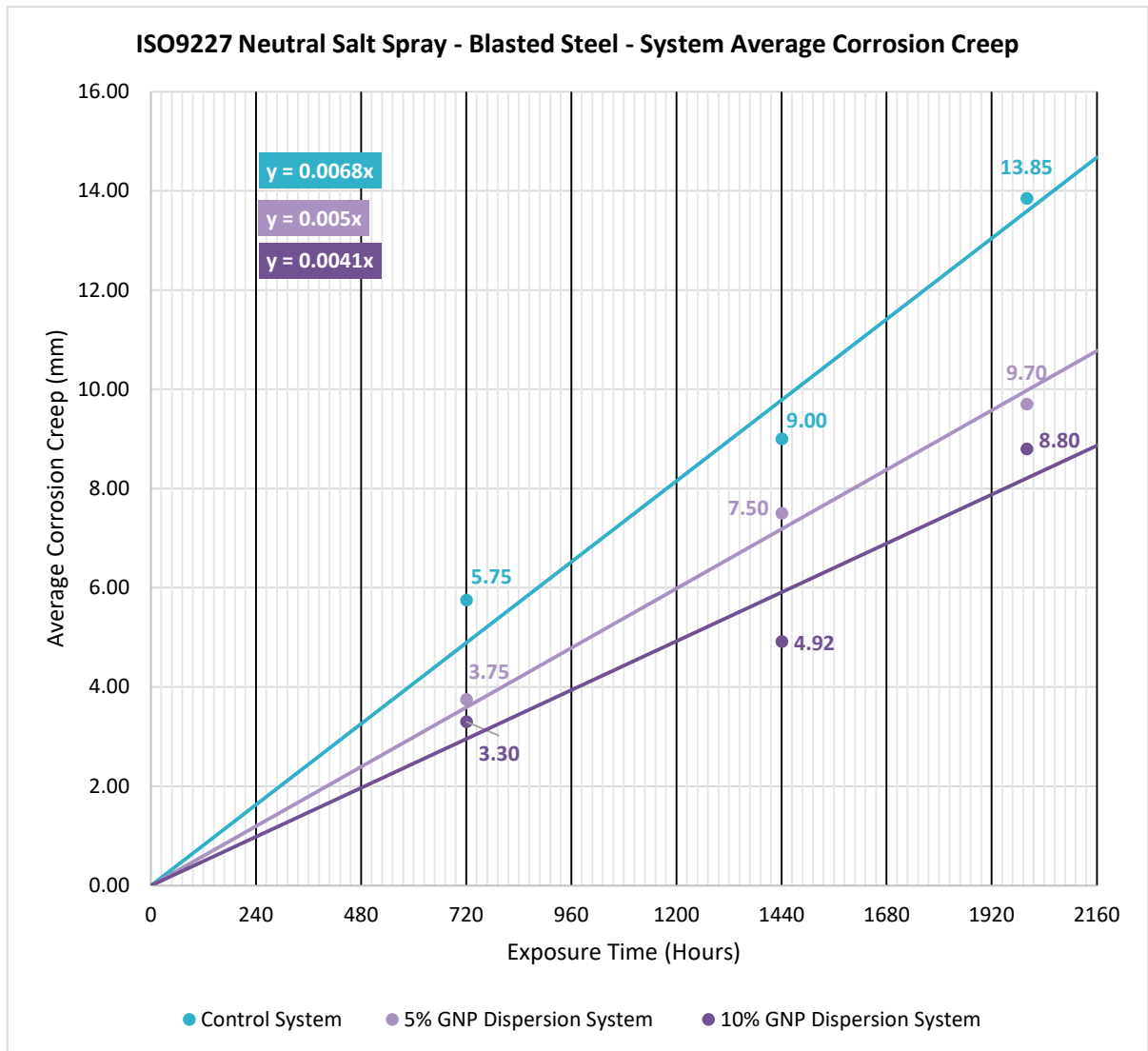


Figure 4 – ISO9227 Neutral Salt Spray – Average Corrosion Creep vs. Exposure Time

System	Blister Rating						Location
	Micro	Size 1	Size 2	Size 3	Size 4	Size 5	
Control System	3	2.5	2.5	1.5	0.5	0	Widespread
							Widespread
5% GNP Dispersion System	0	0	0.5	2.5	0	0	Widespread
							Widespread
10% GNP Dispersion System	0	0	1	0.5	0	0	Widespread
							Widespread

Table 3 – ISO9227 Neutral Salt Spray (2000 Hours) Blistering Results (Size vs. Density)

The incorporation of **Genable® 1250** into the coating system clearly shows improvement on the blistering resistance of the coatings under **ISO9227 Neutral Salt Spray (NSS)** conditions as shown in **Figure 3 and 4**. Looking at the data presented (**Table 3**), the **Genable® 1250** systems show an improvement in density of blistering, eliminating some of the size categories when compared to the control.

It is matter of conjecture whether the size or density of the blistering is the determining factor when assessing blistering samples. Increased density in some views infers a larger volume of water penetration through the coating to the underlying substrate, especially when considering the location of said blistering. Widespread blistering shows somewhat uniform penetration, whereas clustered blistering can highlight weak areas, either due to comparatively low DFT or due to intentional defects such as scribes. Seen in the data presented here, the widespread nature of the blistering shows a more uniform penetration of water and ionic salts, so the density of the blistering is a good indication of system performance.

With this in mind, both the **Genable® 1250** systems show improvement over the control for blistering resistance as they lower the density rating of blistering when compared to the control formulation. The 10% **Genable® 1250** loading shows the greatest improvement of the three formulations tested, reducing the density of all size categories.

4. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) has been used extensively for the past two decades to study corrosion of metal substrates and coating performance. EIS is able to provide additional insights and measurements into the mechanism and onset of corrosion.

Panels were tested using a dual approach that combines NSS with EIS testing. Using the combination approach has the benefit of indicating differences in coating behaviour early in testing, where a visual assessment of corrosion would show no difference. In a review paper concerning the performance of fast-cure epoxies for pipe and tank linings, O'Donoghue et al¹ describe the use of EIS as a screening tool, where the coating impedance measured at a frequency of 0.1 Hz can be used for screening materials. In the study, the team assigns impedance values less than 10^6 Ohm.cm^2 to poor coatings and impedance values of 10^{10} Ohm.cm^2 and above to excellent coatings. Between these values, a good coating would represent an impedance value in the order of 10^8 Ohm.cm^2 , with barrier protection beginning at 10^6 Ohm.cm^2 .

Panels were prepared as detailed. After the 7-day cure schedule, initial measurements were taken on EIS, after which, samples were put on NSS and removed at intervals for measurement. All electrochemical measurements were recorded using a Gamry 1000E potentiostat in conjunction with a Gamry ECM8 multiplexer to permit the concurrent testing of up to 8 samples per run. Each individual channel was connected to a Gamry PCT-1 paint test cell, specifically designed for the electrochemical testing of coated metal substrates.

Within each paint test cell, a conventional three-electrode system, the coated steel samples represented the working electrodes, a graphite rod served as a counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. The test area of the working electrode was 14.6 cm^2 . All tests were run using a 3.5 wt.% NaCl electrolyte. Electrochemical measurements consisted of corrosion potential measurements, E_{corr} , followed by electrochemical AC impedance spectroscopy (EIS) measurements.

During all EIS experiments, an AC voltage of 10 mV was applied across the sample, with a zero-volt DC bias, over a frequency range of 1 MHz to 0.05 Hz. Ten measurements were recorded for every decade in frequency. An integration time of 1 second per measurement was used with a delay time of 0.2 seconds between each measurement.

The impedance data, shown for all coatings in **Figure 7**, shows that the higher impedance coating was that of the A-GNP35 higher loading sample, followed by the lower loading A-GNP35 sample, suggesting both A-GNP35 samples possess better barrier properties over the control sample. While impedance falls in all cases the high loading of A-GNP 35 remains above the 10^6 Ohm.cm^2 limit set by O'Donoghue et al. The lower loading of A-GNP35 reaches this critical value beyond the 1440hour limit set for C2-3 type environments ISO12944-2 and typically well beyond the performance of the control. This is something which is also reflected in the water uptake data shown in **Figure 8**.

In order to further examine the coated panels for evidence of electrolyte at the coating/substrate interface, equivalent circuit modelling was carried out on the impedance data relating to all coated panels. Interfacial electrolyte may give rise to a Helmholtz or electrical double layer. This electrostatic region is a source of charge density, which may be measured as a capacitance; the presence of a double layer capacitance indicates a full or partial breach of the coating, resulting in electrolyte at the substrate coating interface.

It was found that two different equivalent circuit models could be used to model the entirety of the impedance data, as depicted in **Figure 5** and **Figure 6**.

The elements which make up model 2 (**Figure 6**) include R_{soln} (the resistance of the electrolyte), C_c (coating capacitance), R_{po} (pore resistance), C_{cor} (double layer CPE) and R_{cor} (corrosion resistance). The coating capacitance and pore resistance elements are properties associated with the coating itself, whereas the double layer capacitance and corrosion resistance are both interfacial properties and exist when electrolyte meets the metal surface. Greater double layer CPE values indicate a larger presence of electrolyte at the interface, and, potentially, greater levels of corrosion.

It is typical to use a constant phase element (CPE) in place of a pure capacitor for the determination of double layer capacitance since such capacitive behaviour often carries elements of non-ideality; the CPE is a more appropriate fit for such modelling.

Model 1 (**Figure 5**), a Randles type circuit, is essentially the same as model 2, but without the additional time constant (incorporating double layer CPE and corrosion resistance). Therefore, we would expect to use model 1 in cases where the coating has not been breached to any extent e.g. early on post NSS exposure, and use model 2 in cases where the coating has been breached.

For all samples it was found that model 1 was the more appropriate fit up to ~300 hours, suggesting no double interfacial layer up to ~300 hours NSS exposure, and no breach of the coatings. Beyond this point, for all samples, it was found that model 2 was the more appropriate fit, suggesting some level of interfacial electrolyte for all samples beyond ~300 hours (to varying degrees). The emergence of the double layer CPE at ~300 hours NSS exposure is highlighted in **Figure 9**. **Figure 9** shows the progression of the double layer CPE over the course of the experiment. In the stages of exposure up to ~1150 hours, both of the A-GNP35 samples show a relatively low double layer CPE that is lower than the control. This suggests a relatively low amount of electrolyte is present at the interface, indicating a superior barrier performance. The lowest CPE values were seen for the higher loading A-GNP35 sample, followed by the lower loading A-GNP35 sample. In respect of CPE, the 0.1 wt.% A-GNP35 sample gave a similar end point CPE value to that of the 0.05 wt.% A-GNP35 sample.

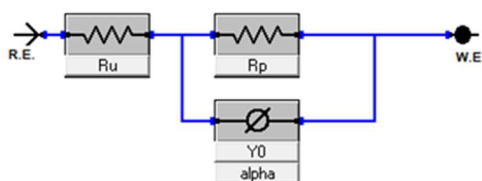


Figure 5 – Equivalent circuit model 1 - Initial model - Single time constant

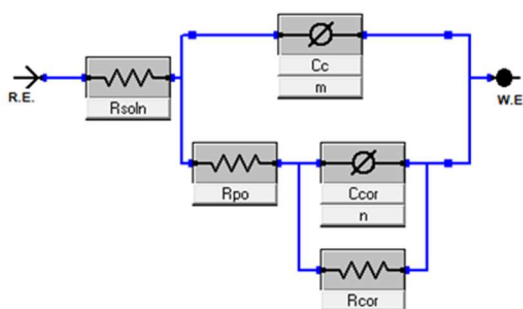


Figure 6 – Equivalent circuit model 2 - later model including double layer CPE

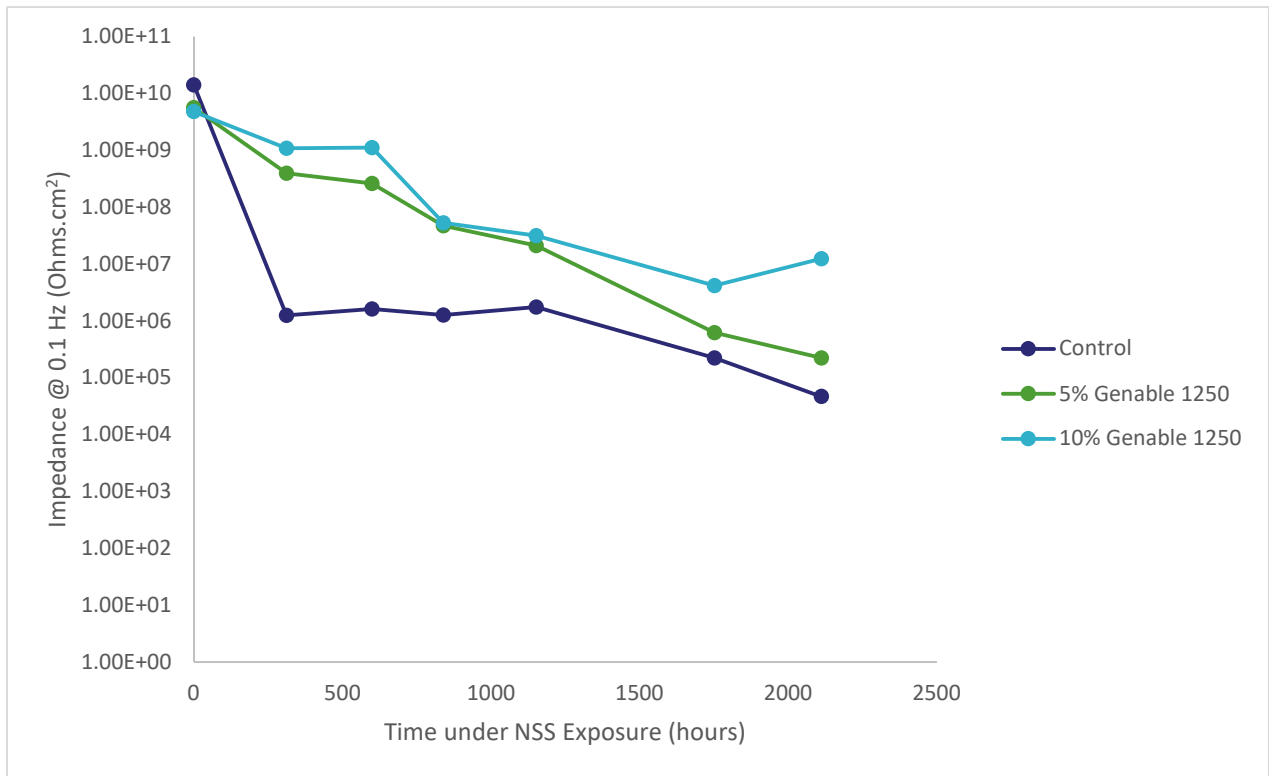


Figure 7 – Impedance @ 0.1 Hz Vs time under NSS exposure

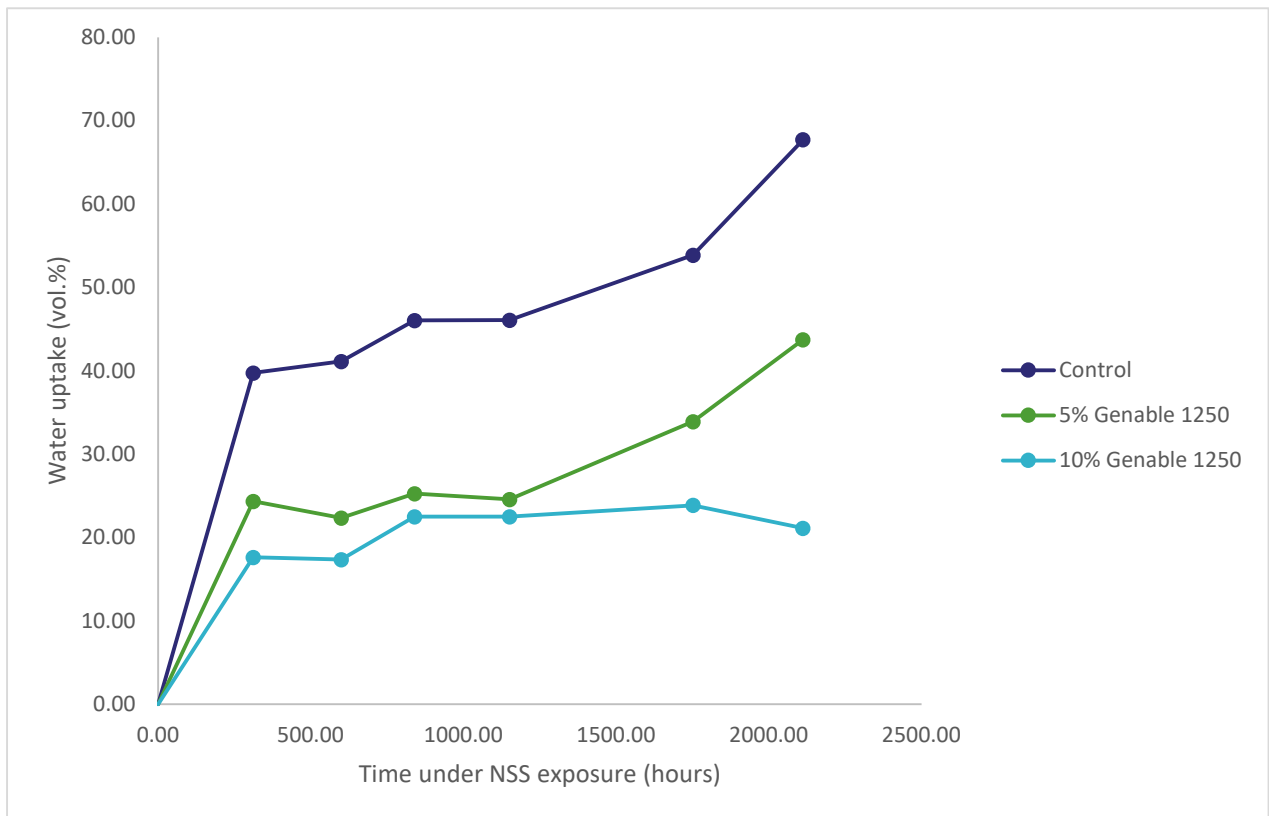


Figure 8 – Water uptake Vs time under NSS exposure

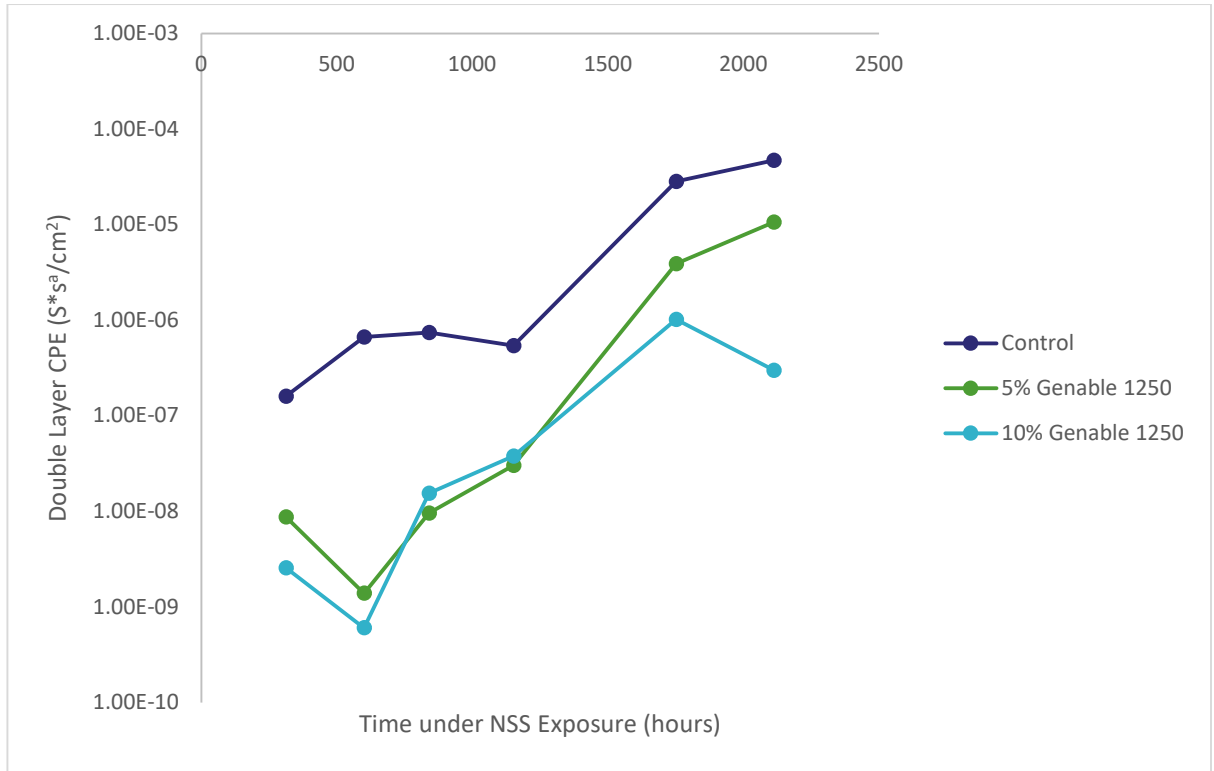


Figure 9 – Double layer CPE Vs time under NSS exposure

5. Mechanical Property Evaluation

Mechanical properties were assessed through direct impact and adhesion performance.

5.1. Adhesion Testing

System	Classification	
	Test 1	Test 2
Control	0	0
5% <i>Genable</i> ® 1250 Dispersion	1	1
10% <i>Genable</i> ® 1250 Dispersion	1	1

Table 4 – Crosshatch Adhesion Results

System	Classification	
	Test 1	Test 2
Control	8	8
5% <i>Genable</i> ® 1250 Dispersion	8	8
10% <i>Genable</i> ® 1250 Dispersion	8	8

Table 5 - Penknife Adhesion Results

The incorporation of *Genable*® 1250 into the system appears to have a marginal effect on the adhesion of the coating to the substrate compared to the control. This is, however not reflected when the systems undergo penknife adhesion test (**Table 4 and 5**).

5.2. Impact Testing

The dropping of a 1 Kg round tipped weight from various heights to test the resistance to cracking and fracturing through direct impact to the surface of the coating. It should be noted that none of the coatings failed under the impact stress (no cracking of the coating).

System	Impact Height (cm) 1 Kg Weight								
	10	20	30	40	50	60	70	80	90
Control	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
5% <i>Genable</i> ® 1250 Dispersion	Pass	Pass	Pass	Pass	Pass	Pass	Deformed	Deformed	Deformed
10% <i>Genable</i> ® 1250 Dispersion	Pass	Pass	Pass	Pass	Pass	Pass	Deformed	Deformed	Deformed

Table 6 - Impact Resistance Results

In the data displayed (**Table 6**), a pass indicates the coating received no visible damage in the way of cracking, deformed means that the coating was affected by the impact in some way but no damage in the form of cracking. A fail, although none were present in this round of testing, would be damage to the coating by way of cracking, fracturing or loss of material from the surface of the substrate.

6. Discussion

When comparing the average corrosion creep results for both ASTM G-85-94 Prohesion and ISO9227 Neutral Salt Spray, both of the graphene loaded systems perform better in terms of corrosion resistance when compared to the standard control system. The higher 10% loading of **Genable® 1250** offers the greatest increase in corrosion resistance, achieving the lowest amount of corrosion of the three tested systems up to 2000 hours of exposure. This loading shows a reduction in average corrosion of 43.1% and 36.5% at 2000 hours under ASTM G-85-94 Prohesion and ISO9227 Neutral Salt Spray test conditions respectively. Likewise, both systems show a lower average rate of corrosion when compared to the control, as seen from Figure 2 and Figure 4.

In terms of blistering, whilst the ASTM G-85-94 Prohesion test data Table 2 offers little in the way of conclusive evidence in favour of one system or another (likely due to the dry cycle of the test method itself), some conclusion can be drawn from the data under ISO9227 Neutral Salt Spray conditions Table 3. The blistering should be taken as a relationship between the density and size rating. The **Genable® 1250** samples tend to show a lower density of blistering occurring, however the blistering that does occur tends to sit around the size 2/3 rating. The control samples on the other hand, show a wider range of blistering, from micro up to size 4 in this case, with again a wider range of density ratings, from low density to moderately high. Singular or low-density blistering, regardless of size, could be indicative of lower and less widespread water and ionic salt permeation through the coating to the steel substrate below. Although larger sized blisters in their own right are not to be overlooked (though still within the range of the control system), the reduction in density and elimination of some size categories is indicative of performance enhancement.

It is useful to contrast the ASTM G-85-94 Prohesion and ISO9227 Neutral Salt Spray exposure performance with the EIS output data. As indicated, the emergence of the double layer CPE at approximately 300 hours NSS exposure is highlighted in Figure 9. This also shows the progression of the double layer CPE over the course of the experiment. In the stages of exposure up to approximately 1150 hours, both of the **Genable® 1250** samples show a relatively low double layer CPE, indicating a superior barrier performance. This is also reflected in the impedance data in Figure 7. EIS data is confirming the low average creep seen on salt spray exposure and the improvement in barrier performance.

Mechanically, **Genable® 1250** systems demonstrate a slight reduction in mechanical resistance to various sources. The **Genable® 1250** systems do not fail the tests; however, some deformation is present under impact testing conditions together with minor loss of adhesion to the substrate. This does not appear to have any negative effect on the anti-corrosion performance as previously demonstrated and could likely be offset by the inclusion of other mechanical property enhancing additives such as adhesion promoters.

In looking at the data presented above, it is important to recognize that the formulations evaluated are simple starting point formulations. Several formulating steps may be taken to improve the overall performance of the systems.

Coalescence: Waterborne epoxies are complex heterogeneous systems. The epoxy system used is a solid epoxy dispersion. At the point of film formation, the epoxy particles and curing agent particles must coalesce so that proper cure can occur. Coalescence may be enhanced through use of cosolvents. Glycol ethers are the most versatile however the list below are commonly used:

propylene glycol monomethyl ether (PM)
propylene glycol propyl ether (PnP)
dipropylene glycol n-butyl ether (DPnB)
propylene glycol phenyl ether (PPh)
tripropylene glycol n-butyl ether (TPnB)
ethylene glycol propyl ether (EP)
ethylene glycol butyl ether (EB)
diacetone alcohol (DAA)
dipropylene glycol methyl ether (DPM)

Adhesion Promoters: Epoxy and acrylic functional silanes may provide improved adhesion in the case of cold rolled steel, aluminium and galvanised steel, but generally offer less effectiveness on blasted and phosphate steels.

Anti-corrosion Pigments: It is important to remember that Graphene is being used as a barrier pigment offering increased tortuosity and reduced permeability to salts and their corrosive potential. For optimum corrosion performance GNPs should be used with an anti-corrosive pigment. In selection of a pigment it is important to balance the pigment solubility to obtain the maximum synergy with GNP use. GNP use will extend pigment performance through reduced water uptake, use of partially soluble pigments will ensure that their passivating effect is present for longer potentially extending coating performance. Typical anti-corrosive pigments used in waterborne epoxy systems include:

Zinc Phosphate complex
Zinc Silicate modified aluminium triphosphate
Strontium phosphosilicates
Calcium ion exchange silica
Calcium phosphates

7. Conclusion

The introduction of GNPs and in particular the 10% loaded **Genable® 1250** systems, offers an increase in corrosion performance as measured by average creep. The slight loss of mechanical resistive properties does little to affect the overall corrosion resistance of the system when compared to other graphene and control systems. The extension of the above starting point formulation as indicated to improve coalescence, adhesion to substrate and critically the addition of an anti-corrosive pigment system will assist in meeting corrosion performance requirements for hidden and visible steel work in medium risk environments.

8. References

1 M. O'Donoghue et al: JPCL-PMC (1998), p. 36-51

9. Contact Details

For further information, please contact the Business Development department using the following details:

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