

Anticorrosive Performance of Novel Water based Systems using Graphene Nanoplatelets

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ABSTRACT

Graphene as a 2D nanomaterial has been extensively researched as a new additive to improve barrier performance, reducing corrosion and extending service life. Significant uplifts in anticorrosive performance in solvent based coatings through the use of graphene nanoplatelets has previously been demonstrated, presenting new opportunities for improved protective coatings with extended service life. However, water-based coating development remains a key focus for industry formulators where there is an ongoing effort to reduce the release of volatile organics and achieve comparable anti-corrosion performance to that seen in solvent based systems. To date the, dispersion of graphene in water-based systems has been problematic, causing coating instability or requiring large amounts of surfactant. The authors report a breakthrough technology enabling easy dispersion in water-based coatings while delivering improved corrosion performance. This development provides an important step to raising waterborne coating anti-corrosion performance and extension of water-based system use.

Keywords: graphene, nanomaterial, barrier performance, water based, epoxy, dispersion

INTRODUCTION

Graphene was first isolated in 2004 by Andre Geim and Konstantin Novoselov at Manchester University. They used sticky tape to remove single layers from the surface of graphite and deposit them on a silicon wafer. The isolation of graphene was a breakthrough for which Geim and Novoselov ultimately won the 2010 Nobel prize for Physics. In its purest form, graphene possesses an unsurpassed combination of electrical, mechanical and thermal properties, which gives it the potential to replace existing materials in a wide range of applications and, in the long term, to enable new applications. Graphene's unique two-dimensional structure in the nanoplatelet form results in very high aspect ratio, high surface area materials which are particularly suited for use as multi-functional additives in paints and coatings formulations. Typical current barrier type lamella pigments used within coatings, such as glass flake and micaceous iron oxide, offer a much lower aspect ratio compared with graphene materials, which results in a reduced tortuosity factor and diffusion path length within the coating. Through the use of graphene materials, a superior diffusion path length can be achieved at much lower loading levels compared to traditional barrier additives.

Applied Graphene Materials UK Ltd. (AGM)[†] produces a range of dispersions of graphene nanoplatelets (GNPs), enabling property enhancement. The company has previously reported the development of solvent-based epoxy primer systems utilizing graphene nanoplatelets demonstrating increased performance life¹. It has been demonstrated that GNPs, both as prepared and chemically functionalized, when incorporated into an organic coating system or host matrix, provide a highly tortuous pathway which acts to impede the movement of corrosive species towards the metal surface², a passive corrosion protection mechanism. In support of this, previous work has also shown that very small additions of GNPs decreased water vapor transmission rates³, indicating a barrier mechanism, while some authors also report electrochemical activity provided by graphene within coatings⁴.

Water-borne technology has seen growth as interest in sustainable products with reduced environmental impact has increased. This is evidenced by increasingly stricter environmental regulations and growing end user demand for environmentally friendly technology. Despite the advances in waterborne solutions, high performance anticorrosion coatings remain largely solvent borne because of the requirement for high chemical and weather resistance that cannot yet be achieved with water-based coatings. However, water-borne direct to metal systems 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 and rail cars. Water-borne epoxy primers in conjunction with polyurethane top-coats are utilised in C2-3 type environments as specified in ISO12944-2, which deals with classification of the principal environments to which steel structures are exposed, and the corrosivity of these environments. Water borne epoxy primer systems may also be used on IH C3-C medium risk environments for hidden steelwork or IV-C3-C for visible steelwork.

For this work, we look to report on the coating performance benefit when GNPs are incorporated into a water-based epoxy primer, with a particular focus on improving anticorrosion performance. GNPs will be incorporated into the epoxy base via commercially available stabilized graphene dispersion products. Assessment of anticorrosion performance takes a dual approach: the more traditional visual accelerated technique of neutral salt spray testing (NSS) combined with electrochemical AC impedance spectroscopy (EIS), with shared test panels across both experiments. These 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 changes noted from the examination of the test panels, providing quantitative data. In addition, 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. Test data from EIS and salt spray test results may also be used to corroborate coating performance.

There have been several reported pieces of work which go some way to exploring the links between laboratory-based accelerated type testing, such as prohesion, neutral salt spray, hydrostatic electrochemical testing, and 'real world' performance and coating lifetime predictions. Such real-world performance data is typically obtained from outdoor exposure techniques under a variety of different exposures e.g. subtropical, and may be both time intensive and costly. As part of a study, using coated steel substrates, Contu et. al. compared short term electrochemical test data (corrosion potential, linear polarization and EIS) to field exposure data in an attempt to rationalize correlations between test types⁵. The study found that for 79% of the coating systems tested, 18 month beachside exposure results could be predicted by electrochemical laboratory tests obtained within 7 days⁵.

[†] Trade name

EXPERIMENTAL PROCEDURE

Material & Sample Preparation

A GNP-free epoxy prototype base (control) coating (part A) was initially prepared, formulated to be representative of a typical water based epoxy primer, as outlined in Table 1. Prior to applying the coating, an amine hardener was added as the part B.

Table 1
Formulation outline of the Control System and GNP-incorporated Systems

Part A: Epoxy Base			
Raw Material	Weight%		
	Control System	5% GNP Dispersion System	10% GNP Dispersion System
Waterborne Epoxy (57% WA)	34.45%	36.35%	38.02%
Dispersing Agent	1.34%	1.41%	1.48%
Defoaming Agent	0.26%	0.27%	0.28%
Talc	4.81%	5.07%	5.31%
Ti Pigment	16.91%	12.14%	7.62%
Yellow Fe Pigment	0.21%	0.15%	0.10%
Black Fe Pigment	0.69%	0.49%	0.31%
Barium Sulphate	13.22%	9.49%	5.96%
Water	11.85%	12.51%	13.08%
Thickener	0.60%	0.63%	0.66%
GNP Dispersion	-	5.00%	10.00%
Flash Rust Inhibitor	1.00%	1.00%	1.00%
Part B: Curing Agent			
Waterborne Curing Agent (55% WA)	13.12%	13.85%	14.48%
Water	1.54%	1.64%	1.70%
Total =	100.00%	100.00%	100.00%
<i>Note: Weight% are based on the full system loading, Part A + Part B</i>			
PVC	31.47%	31.47%	31.48%
Graphene Loading	0.00%	0.025%	0.05%

Prior to coating application, all substrates were degreased using acetone. Each coat was applied to grit blasted mild steel panels (Impress North East Ltd[†]), of dimensions 150 x 100 x 2mm, using a drawdown bar. All panels were permitted a final curing period of 7 days at 25°C (+/-2°C) (Table 2).

[†] Trade name

Table 2
Substrate and Coating Details

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)

A range of tests were carried out to determine suitability of the graphene modified water based primers for use as anticorrosive primers, namely:

- Neutral salt spray – ISO 9227⁶
- Prohesion Testing - ASTM G-85 Annex 5⁷
- Electrochemical Impedance Spectroscopy (EIS)
- Flexibility (Conical Mendrel Bend Test) – ISO 6860:2006⁸
- Rapid Deformation Impact Resistance - ISO 6272-2:2011⁹
- Cross Cut (Adhesion) Test – ISO 2409:2013¹⁰

While neutral salt spray has an established track record in the testing of anticorrosion coatings, studies have shown that prohesion testing can give closer correlation to longer term exterior exposure. By using both neutral salt spray and prohesion testing, we are able to benchmark this new technology against existing technologies, as most anticorrosion coating technologies have been tested against neutral salt spray while getting prohesion data which should give us a better understanding of expected in service performance.

RESULTS

Neutral Salt Spray (NSS) testing

The panels were placed in a corrosion chamber, running ISO 9227⁶ for a period of up to 2000 hours. Two panels of each type were tested and mean values for creep are reported. This test method consists of a continuous salt spray mist at a temperature of 35°C. Panels were assessed at regular intervals (720, 1440 and 2000 hours) for signs of blistering, corrosion, and corrosion creep in accordance with ISO4628¹¹.

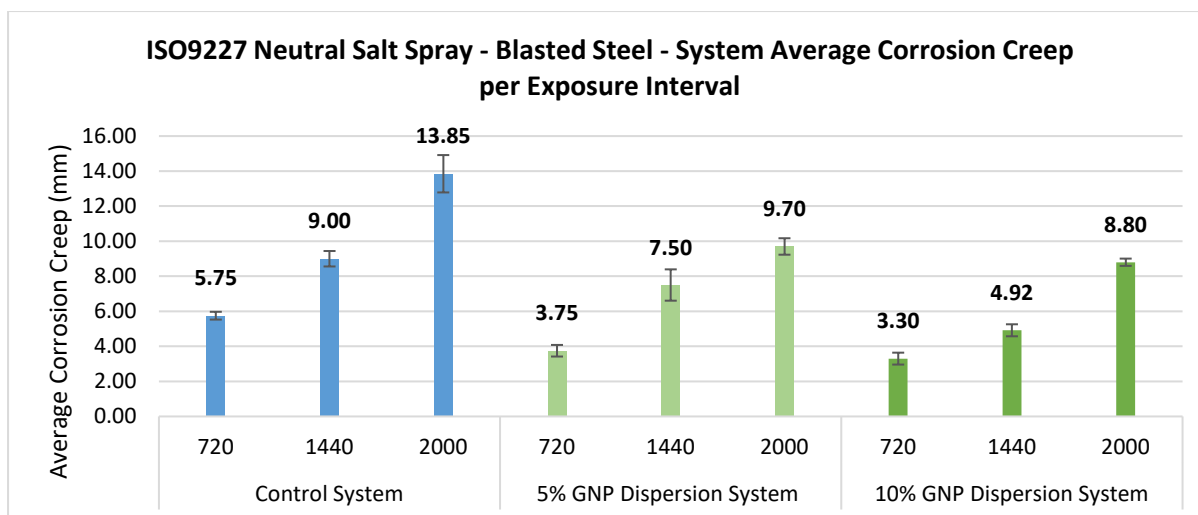


Figure 1: Average Corrosion Creep on NSS Testing

As shown in Figure 1, the inclusion of graphene showed a reduction in corrosion creep for both graphene modified systems, with the higher loaded formulation showing the best performance. Furthermore, coatings containing graphene also showed a lower tendency to blister, as shown in Table 3 below.

Table 3
Blister rating after 2000 hours of testing

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

Prohesion (Cyclic Salt Spray) testing

Panels were placed in a corrosion chamber, running to ASTM G85 Annex 5⁷ Prohesion testing, for a period of up to 2000 hours. This test method consists of cyclic wet and dry periods. Panels were assessed at regular intervals (240, 480, 1440 and 2000 hours) for signs of blistering, corrosion, and corrosion creep in accordance with ISO4628¹¹.