



# **APPLIED GRAPHENE MATERIALS**

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## **TECHNICAL APPLICATION NOTE**

### **Anti-Corrosion Primers: Part 4**

### **Anti-Corrosive Additives for Aluminium Substrates**

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## 1. Introduction

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

AGM has 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**<sup>®</sup> 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-corrosion performance of an epoxy coating. (This improvement is discussed in more detail in AGM's Technical Application Note on Anti-Corrosion Primers: Part 1).

This technical application note describes in further detail how the addition of a **Genable**<sup>®</sup> 2000 series dispersion to a base paint can lead to significant improvements in the anti-corrosion performance of a primer on aluminium substrates, and the potential benefits this can provide for a customer.

## 2. The Protection of Self-Passivating Metals

This application note refers to the use of **Genable**<sup>®</sup> products for the corrosion protection of metallic substrates such as, but not limited to, aluminium and aluminium alloys.

'Active' metals are reactive metals which form a non-adherent and porous oxide/hydroxide layer. The non-adherence of this layer prompts the repeat exposure of bare metal to corrosive species, permitting continued corrosion and degradation of the metal. Passivating metals, such as aluminium and its alloys, readily form a stable and unreactive surface coating with substances such as water and oxygen, thus protecting the metal from further corrosion.

Under normal conditions of pH and oxygen concentration, passivation of self-passivating metals will proceed, as indicated in Pourbaix diagrams (potential/pH diagram demonstrating the regions of thermodynamic stability for a metal/aqueous combination). Outside of such conditions passivation will not occur and, in some cases, the passivation layer may start to break down. In such situations, unprotected aluminium will corrode and largely vanish over periods of exposure as short as a few years. Protection for such metals would ideally include a barrier property to prevent ingress of corrosive species allied to the ability to quickly reform any damage to the natural passivation layer, especially in response to passivation breakdown situations.

Traditionally, self-passivating metals have been protected from oxidation through anodization and alloying with other metals, although anodizing is not generally suited to large scale applications. Anti-corrosive inhibitive coatings may also be applied to either untreated or anodized aluminium surfaces. The active constituents of such coatings are typically marginally water soluble and produce active species which inhibit the ongoing corrosion of the metallic substrate. The active constituents historically have been chromates but other species such as phosphates, molybdates, nitrates, borates and silicates are also used. The selection of active constituents is increasingly subject to regulatory pressures due to increased concerns for the environment and health and safety. Chromates may also be used in the preparation conversion coatings for aluminium. Such regulatory demands has increased the drive towards new inhibitive pigments for coatings.

Graphene has been demonstrated to be electrically conductive, graphene current density is 1,000,000 times greater than copper and its intrinsic mobility is 1,000 times more conductive than silicon. Graphene nanoplatelets, however, when dispersed in a matrix offer significantly reduced conductivity required to

achieve the percolation threshold prior to achieving any meaningful conductance. It is well known that aluminium and its alloys in contact with carbon fibre might exhibit galvanic corrosion, see Figure 1.

Anodic (Corrodes)	Cathodic																			
	Magnesium & Alloys	Zinc & Alloys	Aluminum & Alloys	Cadmium	Steel (Carbon)	Cast Iron	Stainless Steels	Lead, Tin & Alloys	Nickel	Brasses, Nickel-Silvers	Copper	Bronzes, Cupro-Nickels	Nickel Copper Alloys	Nickel-Chrome Alloys	Titanium	Silver	Graphite	Gold	Platinum	
Magnesium & Alloys	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Zinc & Alloys	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Aluminum & Alloys	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Cadmium	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Steel (Carbon)	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Cast Iron	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Stainless Steels	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Lead, Tin & Alloys	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Nickel	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Brasses, Nickel-Silvers	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Copper	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red
Bronzes, Cupro-Nickels	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red	Red
Nickel Copper Alloys	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red	Red
Nickel-Chrome Alloys	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red	Red
Titanium	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red	Red	Red
Silver	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red	Red	Red
Graphite	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Red
Gold	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Platinum	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green

Figure 1. Table indicating potential galvanic risk associated with mixed metals

The carbon (more noble or passive) materials are described as acting in a cathodic manner while the aluminium (more active material) is described as acting in an anodic manner based on the relative position of graphite (carbon) in the galvanic series. Consequently, when both are submerged in the same electrolyte e.g. water, while also electrically connected by some external conductor, the less noble (more active) metal will experience galvanic corrosion. Aluminium and its alloys under these conditions will generate a non-adherent and porous oxide/hydroxide layer. It might be expected that graphene incorporated into a protective film might offer the possibility of a dual functionality on aluminium and it's alloys namely improved barrier performance and promotion of self-passivation dependent on the loading level used.

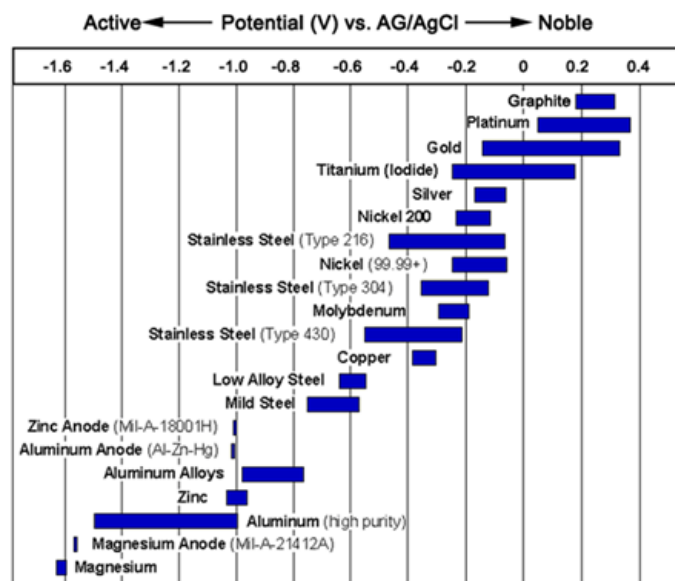


Figure 2. Galvanic series comprising several metals, alloys and graphite

### 3. Anti-Corrosion Evaluation of Graphene Dispersions

**Genable® 2400** is an active dispersion of a conductive graphene formulated into a simple epoxy resin. A reference and anti-corrosion coating was formulated below\*.

Part	Item	Raw Material Name	Control	Genable® 2400 (1)	Genable® 2400 (2)
<b>A</b>	1	Epoxy Resin (EEW 190g/eq.)	83.333	82.834	78.338
	Charge Item 1				
	2	<b>Genable® 2400</b> dispersion	0	0.5	5
	Add item 2. Mix at medium speed (1000rpm) for 15 minutes				
<b>B</b>	3	Amine Hardener	16.667	16.666	16.662

PVC (%)	<b>N/A</b>	<b>2.67</b>	<b>26.80</b>
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The epoxy to hardener mix ratio can be calculated for an appropriate hardener based upon the EEW and AHEW values. In this case an aliphatic amine hardener was used (e.g. Ancamine 2324).

\*All coatings studied were un-optimised resin-only clears and not fully formulated products. For formulation guidance please contact Business Development on the included contact details.

#### 3.1. Manufacturing Guidelines for Anti-Corrosion Coating

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

When graphene dispersions were post-added into coatings under low shear condition, an overhead stirrer was used with typical conditions of 1000 to 1500 rpm for 10 to 15 minutes.

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

#### 3.2. Test Panel Preparation

<b>Substrate</b>	5005 Grade Aluminium
<b>Dimensions</b>	150 x 100 x 2 mm
<b>Preparation</b>	Degreasing with acetone
<b>Application</b>	Spray application (gravity-fed gun 1.2 mm tip)
<b>Coating Thickness</b>	4-60 microns DFT
<b>Curing</b>	7 Days at Room Temperature

## 4. Testing Carried Out – Potentiodynamic Polarisation Testing

Store under ambient conditions for up to 12 months. Dispersions may show slight sedimentation during transportation or on storage. Customer may need to re-agitate by simply mechanically mixing thoroughly with a spatula, palette knife or mechanical stirrer before use.

Potentiodynamic polarisation scans permit considerable amounts of information on electrode processes to be determined. Through this technique, information on corrosion rate, pitting susceptibility, passivity and anode/cathode behaviour of an electrochemical system may be obtained. During such scans, the driving force of the anodic/cathodic reactions (potential) is varied and the net change in reaction rate (the current) is measured. Tafel plots are usually displayed with the applied potential on the y axis and the logarithm of the measured current on the x axis, where the top half above the corrosion potential represents the anodic portion of the plot and the bottom half below the corrosion potential represents the cathodic portion of the plot.

Samples of the coatings described in section 3 above were studied in both scribed and unscribed form during the potentiodynamic polarisation testing together with an uncoated (bare metal) aluminium 5005 panel.

### 4.1. Test Conditions

<b>Equipment</b>	Gamry 1000E potentiostat & ECM8 multiplexer
<b>Test Cells</b>	Gamry PCT-1 paint test cells
<b>Set-up</b>	Conventional three electrode system
<b>Reference Electrode</b>	Saturated Calomel (SCE)
<b>Counter Electrode</b>	Graphite rod
<b>Working Electrode</b>	Test samples
<b>Test area</b>	14.6 cm <sup>2</sup>
<b>Electrolyte</b>	3.5% NaCl solution
<b>Applied Potential</b>	+/- 250 mV from OCP
<b>Scan rate</b>	0.5 mV/second
<b>Sample Period</b>	1 Second

### 4.2. Assessment of the Scribe Region

As indicated samples of coated panels were evaluated in both the scribed and unscribed form. The scribing of coatings offers an immediate study opportunity of the bare metal substrate in contact with electrolyte and functional coating (triple phase boundary). The study of the triple phase boundary regions, as highlighted in Figure 3, provides the ability to identify any electrochemical influence imparted by coating pigments (graphene) on the corrosion of the metal substrate.

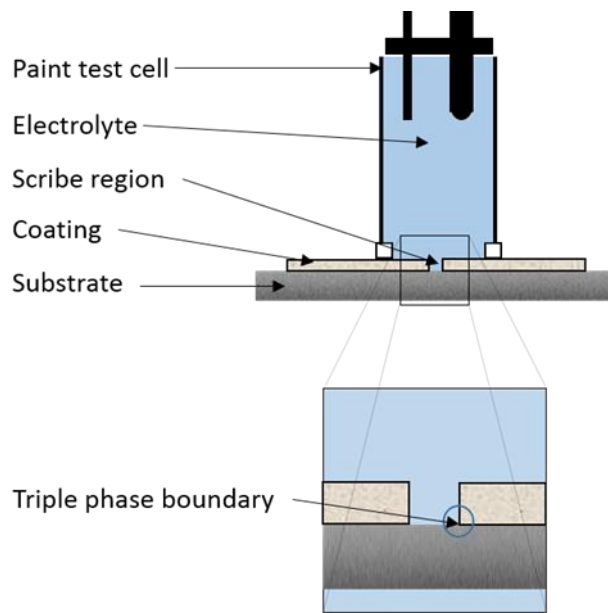


Figure. 3: Schematic of paint test cell used in electrochemical studies with emphasis on the scribe region

## 5. Technical Comments

- No passivation onset was observed for the unscribed or scribed Control sample (no graphene content) during the timescale over which the potentiodynamic scan was run.
- The potentiodynamic scans of the scribed coatings of **Genable® 2400** samples 1 and 2 both showed an onset of passivation
  - ~+213 mV from the corrosion potential for sample 1
  - ~+18 mV from the corrosion potential for sample 2 (Figure 5)

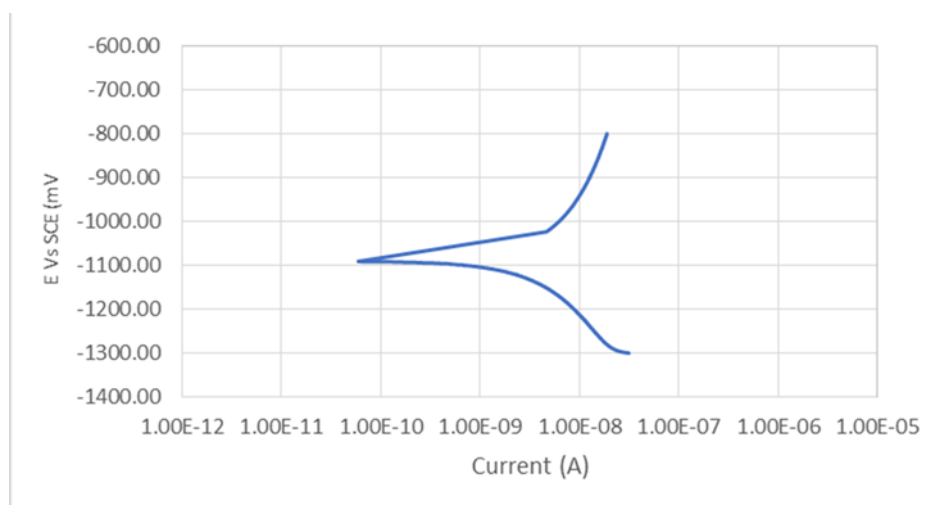


Figure 4: Potentiodynamic scan of a scribed control sample

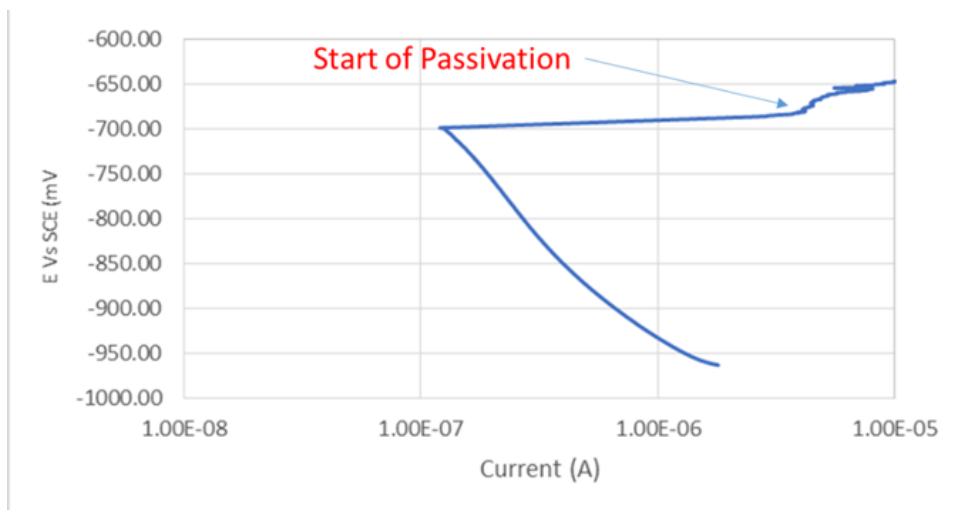


Figure 5. Potentiodynamic scan of a scribed coating of **Genable 2400** sample 2

WVTR and ASTM G-85-94 Prohesion testing previously reported (Technical Application Note on Anti-Corrosion Primers: Parts 1 - 3) strongly suggest that the incorporation of graphene products may offer excellent barrier protection for use in coatings. The incorporation **Genable® 2400** at loadings as low as 0.5 wt.% when applied to aluminium and/or its alloys appears to offer anti-corrosion protection, despite the fact that such low loadings of graphene will offer minimal barrier protection. As indicated by the potentiodynamic scan results, the graphene may be imparting an electrochemical influence on the passivation process.

## 6. Benefits of **Genable® 2000 Series** for the Protection of Self-Passivating Metals

- Stable long-term dispersions designed to be delivered easily into existing manufacturing processes
- Supplied in epoxy resins and can be customised into a variety of common industrial resins
- May be formulated into coating systems suitable for application to: non-surface modified surfaces, anodised substrates (stacked passivation) and conversion coating surfaces
- Chromate and phosphate free additive