Corrosion: Meeting Tomorrows Performance Needs with Graphene Nano-Platelets

Western Coatings Show

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Introduction
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.
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

<table>
<thead>
<tr>
<th>Graphene Nano-Platelets – AGNP-35</th>
</tr>
</thead>
<tbody>
<tr>
<td>• AGM GNPs are manufactured using proprietary and patented bottom up synthesis process</td>
</tr>
<tr>
<td>• Graphene, composed of very thin, crumpled sheets, typically 5-7 atomic layers with approximately 5% oxygen</td>
</tr>
<tr>
<td>• Very low density and high surface area, enabling enhanced corrosion resistance at very low loadings.</td>
</tr>
<tr>
<td>• Recommended active Graphene addition between 0.025% to 0.1% weight of total paint formulation</td>
</tr>
</tbody>
</table>
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

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Control</th>
<th>Graphene DTM</th>
<th>Graphene Primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionised Water</td>
<td>6.1%</td>
<td>6.6%</td>
<td>5.5%</td>
</tr>
<tr>
<td>Dispersant</td>
<td>1.8%</td>
<td>2.0%</td>
<td>1.6%</td>
</tr>
<tr>
<td>Defoamer</td>
<td>0.4%</td>
<td>0.5%</td>
<td>0.4%</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td>26.0%</td>
<td>10.1%</td>
<td>23.4%</td>
</tr>
<tr>
<td>Rheology Modifier</td>
<td>1.7%</td>
<td>1.8%</td>
<td>1.5%</td>
</tr>
<tr>
<td>Alkyd Acrylic Resin</td>
<td>60.3%</td>
<td>65.1%</td>
<td>54.2%</td>
</tr>
<tr>
<td>Ammonia (29%)</td>
<td>0.4%</td>
<td>0.5%</td>
<td>0.4%</td>
</tr>
<tr>
<td>Combination Dryer</td>
<td>0.7%</td>
<td>0.7%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Wetting Agent</td>
<td>0.3%</td>
<td>0.3%</td>
<td>0.3%</td>
</tr>
<tr>
<td>Flow Additive</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.5%</td>
</tr>
<tr>
<td>Anti-Skinning Additive</td>
<td>0.8%</td>
<td>0.9%</td>
<td>0.8%</td>
</tr>
<tr>
<td>Flash Rust Inhibitor</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
</tr>
<tr>
<td><strong>Genable® 1250</strong></td>
<td></td>
<td>10.0%</td>
<td>10.0%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td><strong>Graphene Loading</strong></td>
<td>None</td>
<td><strong>0.05%</strong></td>
<td><strong>0.05%</strong></td>
</tr>
</tbody>
</table>
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, *Genable® 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
Neutral Salt Spray Testing using ISO 9227:

• A ladder study of increasing Genable® 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
With each loading of graphene, a significant reduction in the levels of creep was recorded compared to the control.
Neutral Salt Spray – Visual Assessment

Abraided Steel

Control (No GNP)
PVC: 20

10% Genable® 1250
PVC: 30
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
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
Electrochemical Studies
Electrochemical Impedance Spectroscopy Testing

- Measurements recorded using a Gamry 1000E potentiostat with a Gamry ECM8 multiplexer
- Working electrode test area = 14.6 cm²
- 3.5wt% NaCl electrolyte
- Continuous measurements taken over a 140 hour period.
AC Impedance (EIS) – Zones of Protection

- Excellent Protection
- Good Protection
- Protection Begins
- Poor Protection

Impedance @ 0.1 Hz (Ohm.cm²)

Time (hours)
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.
• The addition of 10% Genable® 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.
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% Genable® 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.
• 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.
Graphene in products used by everybody, everyday