APPLIED GRAPHENE MATERIALS

TECHNICAL APPLICATION NOTE

Anti-Corrosion Primers: Part 2

Hybrid Non-metallic Pigments

Contents

1. Introduction

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

Applied Graphene Materials UK Ltd 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 **G***enable*® 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.)

1.1. Hybrid Anti-Corrosion Pigments

This technical application note describes in further detail how the addition of **G***enable*® dispersions and non-metallic active inhibitor pigments to create a hybrid pigment package which can lead to significant improvements in the anti-corrosion performance of a primer and the potential benefits this can provide for a customer.

2. Inhibitors

An ideal inhibitive coating should form a barrier against water and detrimental ions whilst simultaneously releasing a sufficient quantity of inhibitor. These two requirement are antagonistic in principle and require a balance in the pigment with a dependency on the barrier properties of the coating. The inhibitors used in this work included calcium oxide modified silica, ion exchanged amorphous silica and oxyaminophosphate salts.

Inhibitive coatings are generally applied in the form of primers and are used where the substrate is exposed to atmospheric corrosion and not where the substrate is immersed in water or soil.

The selection of an active pigment has been coming under ever increasing environmental and regulatory pressures leading manufactures to remove and/or reduce the amount of metal salts used in coating systems.

3. Anti-Corrosion Evaluation

The objective of the work in this technical note was to evaluate and determine if graphene nanoplatelets in combination as a hybrid pigment package with non-metallic pigments can enhance the performance of the corrosion protection in coating systems to deliver a meaningful extension of life to a C3 category coating according to ISO 12944**.**

Testing carried out

Accelerated exposure:	Salt Spray testing	ASTM G-85-94 Prohesion
Mechanical Testing:	Flexibility	ISO 6860: 6860
	Impact	ISO 6272-2:2004
	Abrasion	ISO 7784
	Adhesion	ISO 4624

3.1. Typical Graphene-Based Primer Formulation

The evaluation was conducted using the graphene based primer formulation below.

The primer was made up using the formulation below resulting in an 87% stoichiometry. It was cured over seven days at ambient room temperature.

Part A: Epoxy Base

	Item	Raw material name	Weight %		
	Charge items 1,2,3 ,4 and 5 and mix at high speed (2000 rpm) for 10 minutes		**Control**	***Genable®* 1001**	***Genable®* 1201**
	1	Epoxy resin (EEW= 250g/eq.)	11.34	11.34	11.34
	2	Cymel U-216 resin	0.25	0.25	0.25
Charged	3	Anti-terra U	0.41	0.41	0.41
	4	Xylene	7.84	7.84	7.84
	5	Tixogel MP	0.37	0.37	0.37
	Check gel is homogenous and free of bits. Continue mixing if not.				
	Add items 6 to 9. Mix at high speed (2000 rpm) for 15 minutes. Check grind <25 microns and add items 6.				
	6	Butanol	2.02	2.02	2.02
Grind	7	Titanium dioxide	11.18	11.18	11.18
	8	Inhibitive pigments (A or B or C)	0	1	1
	9	Blanc fixe	44.47	44.47	44.47
	Add items 11, 12 & 13. Mix at medium speed (1,000rpm) for 15 minutes.				
	10	***Genable®*** dispersion addition	0	5	10
Let Down	11	Epoxy resin (EEW=250g/eq.)	14.28	8.28	3.28
	12	Xylene	7.84	7.84	7.84

Part B: Hardener

The epoxy to hardener mix ratio can be calculated for an appropriate hardener based upon the EEW and AHEW values.

pvc	35	37	37
VOC (g/l)	320	309	314

3.2. Manufacturing Guidelines for Anti-Corrosion Coating

It is recommended that **G***enable*® 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.

3.3. Test Panel Preparation

Substrate	Cold rolled steel
Dimensions	152mm by 101mm
Preparation	Grit blasting to SA2-1/2 rolled by degreasing with acetone
Grit	Irregularly shaped chrome/nickel shot
Application	Spray application (gravity-fed gun 1.2 mm tip)
Coating Thickness	DFT 60-75 µm
Curing	7 Days at room temperature

4. Salt Spray Testing ASTM G-85-94 Prohesion Results

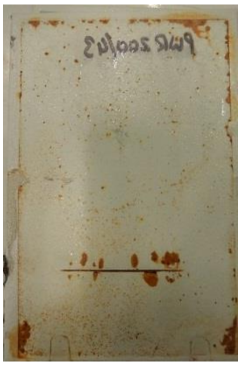
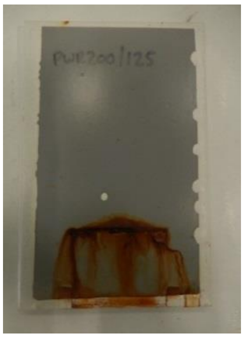
Primer Control, **G***enable*® **1001** and **G***enable*® **1201** test panels after 1000, 2000 & 3000 hours of testing to ASTM G-85-94:

<table>
<tr><th></th><th>Control (Primer Only)</th><th>Control + Genable® 1001</th><th>Control + Genable® 1201</th></tr>
<tr><td>1000 Hours</td><td></td><td></td><td></td></tr>
<tr><td>2000 Hours</td><td>X</td><td>X</td><td></td></tr>
<tr><td>3000 hours</td><td>X</td><td>X</td><td></td></tr>
</table>

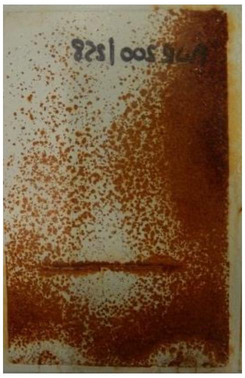
Primer Control, **G***enable*® **1001** and **G***enable*® **1201** test panels (all incorporating Pigment A) after 1000, 2000 and 3000 hours of testing to ASTM G-85-94:

	Control (Primer with Pigment A)	**Control + G*enable*® 1001**	**Control + G*enable*® 1201**
1000 Hours			
2000 Hours	X	X	X
3000 Hours	X	X	X

Primer Control, **G**_enable_® **1001** and **G**_enable_® **1201** test panels (all incorporating Pigment B) after 1000, 2000 and 3000 hours of testing to ASTM G-85-94:

	Control (Primer with Pigment B)	**Control + G*enable*® 1001**	**Control + G*enable*® 1201**
1000 Hours			
2000 Hours	X		X
3000 Hours	X		X

Primer Control, **G***enable*® **1001** and **G***enable*® **1201** test panels (all incorporating Pigment C) after 1000, 2000 and 3000 hours of testing to ASTM G-85-94:

	Control (Primer with Pigment C)	**Control + G*enable*® 1001**	**Control + G*enable*® 1201**
1000 Hours			
2000 Hours	X	X	
3000 Hours	X	X	

4.1. Corrosion Rating Test Results (1000, 2000 & 3000 Hours)

1000 Hours Corrosion Rating Test Results

G*enable*® Addition Level in Wet Primer	**% Graphene in Wet Primer**	**1000 Hours**				**Comments**
		Creep (mm)	**Blistering Quality**	**Size (ISO)**	**Corrosion**	
None (Control)	0	>10	0	S4	Ri5	Corroded across whole face
G*enable*® **1001** at 5%	0.50%	>10	2	S2	Ri5	Corroded across whole face
G*enable*® **1201** at 10%	0.10%	>10	4	S3	Ri5	Small corrosion spots across face
None (Control)	0	>10	0	S0	Ri5	Corrosion spots start
G*enable*® **1001** at 5%	0.50%	1	0	S0	Ri2	Good
G*enable*® **1201** at 10%	0.10%	>10	3	S4	Ri5	Corroded across whole face
None (Control)	0	>10	2	S4	Ri5	Corroded across whole face
G*enable*® **1001** at 5%	0.50%	>10	0	S0	Ri5	Corrosion across half panel
G*enable*® **1201** at 10%	0.10%	<1	0	S0	Ri0	Good

2000 Hours Corrosion Rating Test Results

Primary Anti-Corrosive	**G*enable*® Type & Addition Level in Wet Primer**	**% Graphene in Wet Primer**	**2000 Hours**				**Comments**
			Creep (mm)	**Blistering Quantity**	**Size (ISO)**	**Corrosion**	
Pigment A	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
Pigment A	**G***enable*® **1001** at 5%	0.50%				Ri5	Failed, didn't reach 2000 hours
Pigment A	**G***enable*® **1201** at 10%	0.10%				Ri3	Failed, didn't reach 2000 hours
Pigment B	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
Pigment B	**G***enable*® **1001** at 5%	0.50%	**1**	**0**	**S0**	**Ri2**	**Good**
Pigment B	**G***enable*® **1201** at 10%	0.10%				Ri2	Failed, didn't reach 2000 hours
Pigment C	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
Pigment C	**G***enable*® **1001** at 5%	0.50%				Ri0	Failed, didn't reach 2000 hours
Pigment C	**G***enable*® **1201** at 10%	0.10%	**<1**	**0**	**S0**	**Ri0**	**Good**

3000 Hours Corrosion Rating Test Results

Primary Anti-Corrosive	G*enable*® Type & Addition Level in Wet Primer	% Graphene in Wet Primer	2000 Hours				Comments
			Creep (mm)	Blistering (Qty)	Size (ISO)	Corrosion	
Pigment A	None (Control)	0	/	/	/	Ri5	Failed, didn't reach 2000 hours
Pigment A	**G***enable*® **1001** at 5%	0.50%	/	/	/	Ri5	Failed, didn't reach 2000 hours
Pigment A	**G***enable*® **1201** at 10%	0.10%	/	/	/	Ri3	Failed, didn't reach 2000 hours
Pigment B	None (Control)	0	/	/	/	Ri5	Failed, didn't reach 2000 hours
Pigment B	**G***enable*® **1001** at 5%	0.50%	**1**	**0**	**S0**	**Ri2**	**Good**
Pigment B	**G***enable*® **1201** at 10%	0.10%	/	/	/	Ri2	Failed, didn't reach 2000 hours
Pigment C	None (Control)	0	/	/	/	Ri5	Failed, didn't reach 2000 hours
Pigment C	**G***enable*® **1001** at 5%	0.50%	/	/	/	Ri0	Failed, didn't reach 2000 hours
Pigment C	**G***enable*® **1201** at 10%	0.10%	**<1**	**0**	**S0**	**Ri0**	**Good**

4.2. Mechanical Testing (7 Day Cure): Adhesion, Flexibility, Impact & Abrasion

4.2.1. Adhesion Testing

Primary Anti-Corrosive	G*enable*® Type & Addition Level in Wet Primer	% Graphene in Wet Primer	Force (MPa)			Comment
			Rating 1	Rating 2	Average	
Pigment A	None	0	3.25	2	2.63	85% Adhesive failure
Pigment A	**G***enable*® **1001** at 0.5%	0.50%	2.8	3	2.9	60% Adhesive 40% Cohesive
Pigment A	**G***enable*® **1201** at 0.1%	0.10%	1	1.2	1.1	100% Adhesive
Pigment B	None	0	2.8	2.8	2.8	20% Adhesive 80% Cohesive
Pigment B	**G***enable*® **1001** at 0.5%	0.50%	1.5	1.8	1.65	Glue failure
Pigment B	**G***enable*® **1201** at 0.1%	0.10%	2.25	2.8	2.53	100% Cohesive
Pigment C	None	0	2.5	3	2.75	25% Adhesive 75% Cohesive
Pigment C	**G***enable*® **1001** at 0.5%	0.50%	3.25	3.5	3.38	25% Adhesive 75% Cohesive
Pigment C	**G***enable*® **1201** at 0.1%	0.10%	1	1.25	1.13	95% Adhesive 5% Cohesive

4.2.2. Conical Mandrel Testing

Primary Anti-Corrosive	**G***enable*® **Type & Addition Level in Wet Primer**	**% Graphene in Wet Primer**	**Cracking**	**Elongation**
Pigment A	None (Control)	0	4	21
Pigment A	**G***enable*® **1001** at 5%	0.50%	0	<35
Pigment A	**G***enable*® **1201** at 10%	0.10%	0	<35
Pigment B	None (Control)	0	4	21
Pigment B	**G***enable*® **1001** at 5%	0.50%	0	<35
Pigment B	**G***enable*® **1201** at 10%	0.10%	120	3
Pigment C	None (Control)	0	6	23
Pigment C	**G***enable*® **1001** at 5%	0.50%	120	3
Pigment C	**G***enable*® **1201** at 10%	0.10%	80	5

4.2.3. Impact Testing

Primary Anti-Corrosive	**G***enable*® **Type & Addition Level in Wet Primer**	**% Graphene in Wet primer**	**Cracking begins: Height (cm) 1Kg Weight**						
			10	20	30	40	50	60	70
Pigment A	None (Control)	0							
Pigment A	**G***enable*® **1001** at 5%	0.50%							
Pigment A	**G***enable*® **1201** at 10%	0.10%							
Pigment B	None (Control)	0							
Pigment B	**G***enable*® **1001** at 5%	0.50%							
Pigment B	**G***enable*® **1201** at 10%	0.10%							
Pigment C	None (Control)	0							
Pigment C	**G***enable*® **1001** at 5%	0.50%							
Pigment C	**G***enable*® **1201** at 10%	0.10%							

4.2.4. Taber Abrasion Testing

Primary Anti-Corrosive	**G***enable*® **Type & Addition Level in Wet Primer**	**% Graphene in Wet Primer**	**100 Cycles, 1Kg Weight, CS-10 Discs**			
			Initial Mass (g)	**Final Mass (g)**	**Mass Loss (g)**	**Wear Rating**
Pigment A	None (Control)	0	68.1826	68.1543	28.3	283
Pigment A	**G***enable*® **1001** at 5%	0.50%	67.8742	67.842	32.2	322
Pigment A	**G***enable*® **1201** at 10%	0.10%	66.7089	66.6539	55	550
Pigment B	None (Control)	0	68.0394	68.0097	29.7	297
Pigment B	**G***enable*® **1001** at 5%	0.50%	67.3551	67.3154	39.7	397
Pigment B	**G***enable*® **1201** at 10%	0.10%	67.1761	67.1399	36.2	362
Pigment C	None (Control)	0	67.8543	67.8034	50.9	509
Pigment C	**G***enable*® **1001** at 5%	0.50%	67.2149	67.1692	45.7	457
Pigment C	**G***enable*® **1201** at 10%	0.10%	66.8288	66.7935	35.3	353

5. Technical Comments

5.1. Assessing if Graphene can Enhance Anti-Corrosion Performance

The aim of the work described in this technical application note is to evaluate if graphene nanoplatelets in combination with environmentally friendly and non-zinc inhibitive pigments could enhance the corrosion protection performance of anti-corrosion primers which in turn could lead to a meaningful extension of coating life.

Given that some of the key anti-corrosion pigments such as chromates and phosphates incorporated into coating systems are coming under increasing environmental pressure to be removed or reduced then viable alternatives will be of interest to the Coatings Industry.

This work has demonstrated that graphene in combination with environmentally friendly inhibitive pigments can significantly enhance corrosion protection. Work has also shown they could be added into the primer, intermediate or top coating layer.

5.2. Performance

G*enable*® **1001** and **G***enable*® **1201** have been shown to improve anti-corrosion performance in coating films which are free of defects both singularly and in combination with other anti-corrosive pigments.

Significant improvements are observed when graphene nanoplatelets are used in combination with zinc phosphate and other inhibitors, the corrosion observed at the scribe and across the face of the test panels show significant improvements over traditional anti-corrosive pigments alone (TAN Anti-Corrosion Coatings Part 1). Here we report on a long term series of trials where graphene nanoplatelets are combined in a hybrid manner with non-metallic inhibitors to generate an environmentally friendly solution to corrosion.

Compared to the blank (control) formulation, the inclusion of **G***enable*® **1001** and **G***enable*® **1201** with Type B Pigment provides a substantial improvement in anti-corrosion performance. After 3000 hours the **G***enable*® **1001** formulation continues to perform showing minimal signs of corrosion. The **G***enable*® **1200** dispersion in combination with the Type A Pigment also provided a good level of performance up to 2000 hours. The anti-corrosive free formulation had completely failed after 500 hours, so this represents a six-fold and four-fold improvement in time to failure respectively. The formulation with the Type C pigment demonstrated good performance up to 3000 hours whereas the rest of the sample panels had generally failed completely between 1000 and 2000 hours. Anti-corrosion performance is highly dependent on specific coating formulation; the results seen in prototype may not necessarily be true in different formulations.

Mechanical testing was carried out after 7 days cure on the epoxy based coating to investigate whether graphene had an influence upon the mechanical properties such as flexibility, impact, abrasion and adhesion performance. The test results indicated some variance but the overall effect upon mechanical performance characteristics over the control formulations alone was small.

5.3. Formulating

The substantial programme of work conducted by AGM has led to the development of the **G***enable*® **1000** and **G***enable*® **1200** ranges. This work has been further developed with other inhibitor pigments to produce a hybrid anti-corrosion system. The starting point formulation outlined above is an example of how the **G***enable*® graphene dispersions can be introduced directly into the resin formulation. The dispersions are typically introduced into the formulations at the let-down stage.

6. G*enable*® Storage Stability

6.1. Epoxy

AGM graphene is supplied in dispersion format. 12 months stability testing has shown that dispersions in epoxy resins are stable to agglomeration. Data below for 5% A-GNP10 in liquid epoxy resin dispersion.

	12 months
Syneresis	None
Sedimentation	5mm soft sediment. Easily re-incorporated.
Agglomeration	None

	Dx (10)	**Dx (50)**	**Dx (90)**
Initial	0.83 µm	8.10 µm	31.0 µm
1 month	0.68 µm	7.65 µm	28.8 µm
12 months	0.68 µm	7.27 µm	29.2 µm

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

6.2. Water

Water borne products should be stored in covered, dry conditions and stored in the temperature range 4°C (40°F) and 35°C (95°F).

G*enable*® **1050** has a 3 month shelf life. If settling has occurred during storage simple mechanical mixing will re-disperse graphene sufficiently for testing of samples.

G*enable*® **1250** has a 6 month shelf life with minimal sedimentation expected.

6.3. Solvents

The **G***enable*® **1000** series (A-GNP10 dispersed into standard solvents) have a 3 month shelf life. If settling has occurred during storage simple mechanical mixing will re-disperse graphene sufficiently for testing of samples.

When longer term storage testing of A-GNP10 in MEK was carried out to assess stability, some sedimentation was observed after 3 months. This can be recombined/reconstituted with mechanical agitation for ten to fifteen minutes by using an electric vortex mixer with a Florock vortex mixer blade for example.

For the **G***enable*® **1200** series sedimentation of the A-GNP35 graphene in the solvent is less likely but some pooling of the solvent may occur on the top surface of the sample. If pooling occurs then simple mechanical mixing prior to testing to re-disperse will suffice.