



APPLIED GRAPHENE MATERIALS

TECHNICAL APPLICATION NOTE

Anti-Corrosion Primers

Part 1

Contents

1. Introduction	3
2. Water Vapour Transmission Rates	3
3. Anti-Corrosion Evaluation	4
3.1. Typical Graphene-Based Primer Formulation	5
3.2. Manufacturing Guidelines for Anti-Corrosion Coating	6
3.3. Test Panel Preparation	6
4. Salt Spray Testing ASTM G-85-94 Prohesion Results	7
4.1. Corrosion Rating Test Results (1000, 2000 & 3000 Hours)	10
4.2. Mechanical Testing (7 Day Cure) : Adhesion, Flexibility, Impact & Abrasion	11
4.2.1. Adhesion Testing	11
4.2.2. Conical Mandrel Testing	11
4.2.3. Impact Testing	11
4.2.4. Taber Abrasion Testing	12
5. Technical Comments	12
5.1. Assessing whether Graphene can Enhance Anti-Corrosion Performance.	12
5.2. Formulating	12
5.3. Performance	12
6. Genable® Storage Stability	13
6.1. Epoxy	13
6.2. Water	13
6.3. Solvents	13
7. Contact Details	14

1. Introduction

Applied Graphene Materials UK Limited (AGM) manufacture graphene nanoplatelets 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 in achieving a technical appreciation of this novel technology.

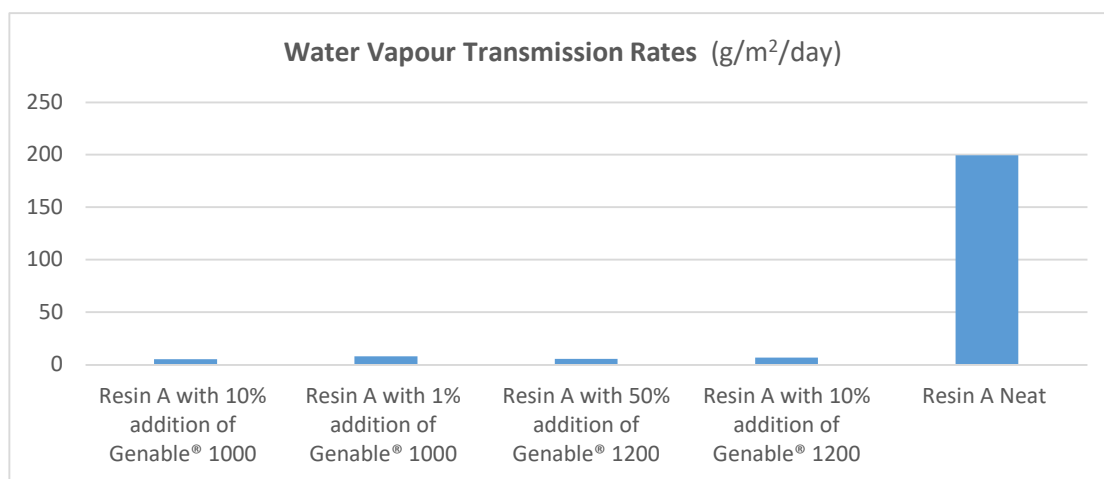
The addition of graphene into coating formulations has demonstrated excellent barrier properties leading to a reduction in water vapour transmission rates (WVTR). This reduction in WVTR significantly enhances the anti-corrosion performance of an epoxy coating.

This technical application note describes in further detail how effective graphene can be in improving the anti-corrosion performance of a primer and the potential benefits this can provide for a customer.

2. Water Vapour Transmission Rates

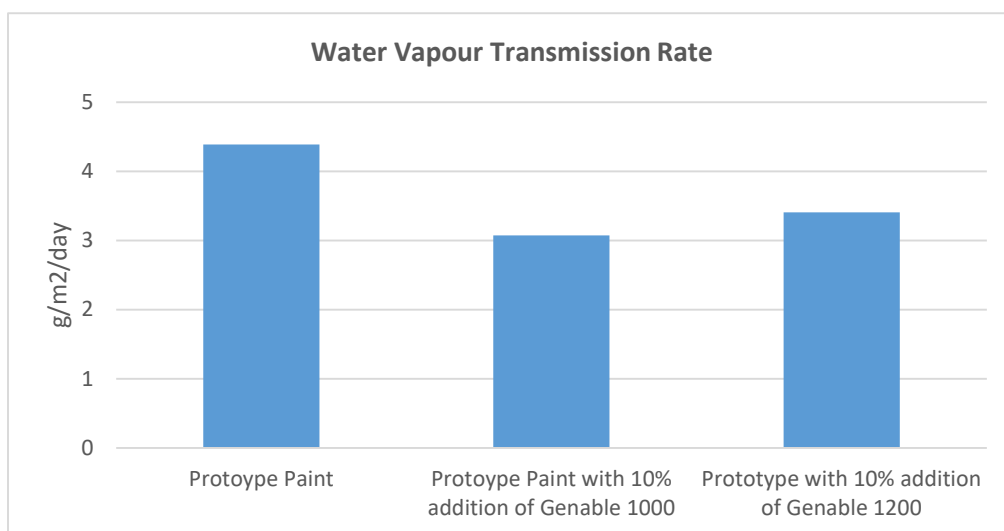
The Water Vapour Transmission Rates (WVTR) of the supplied samples were determined under the guidelines of ASTM D 1653-03 using Test Method B, Condition A.

Testing in clear epoxy resins has demonstrated up to a 97% reduction in WVTR (see chart and table below). Resin A is an epoxy with an EEW of approximately 190 g/eq. cured with a polyamide for 7 days at RT.



Description	WVTR (g/m2/day)	Reduction
Resin A with 10% addition of Genable® 1000	5.2	97.4%
Resin A with 1% addition of Genable® 1000	8	96.0%
Resin A with 50% addition of Genable® 1200	5.6	97.2%
Resin A with 10% addition of Genable® 1200	6.9	96.5%
Resin A Neat	199.5	0%

The introduction of graphene into a pigmented paint formulation resulted in a 30% reduction in water vapour transmission rate when compared to a prototype paint formulation with no graphene.



	WVTR (g/m ² /day)	% Reduction
Prototype Paint	4.386	0%
Prototype Paint with 10% addition of Genable® 1000	3.071	30%
Prototype Paint with 20% addition of Genable® 1200	3.408	22%

3. Anti-Corrosion Evaluation

The objective of the work in this technical note was to evaluate and determine if graphene nanoplatelets can enhance corrosion protection in coating systems to deliver a meaningful extension of life in a Type 3 coating under ISO 12944. The reference anti-corrosion pigment was 8% zinc phosphate.

Testing carried out

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

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

		Weight %		
Item	Raw material name	Control	Genable® 1001	Genable® 1201
Charge	Charge items 1,2,3 ,4 and 5 and mix at high speed (2000 rpm) for 10 minutes			
	1 Epoxy resin (EEW= 250g/eq.)	11.34	11.34	11.34
	2 Cymel U-216 resin	0.25	0.25	0.25
	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.				
Grind	Add items 7 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
	7 Titanium dioxide	11.18	11.18	11.18
	8 (Anticorrosive pigment)	4 to 8 (variable)	4 to 8 (variable)	4 to 8 (variable)
Let Down	9 Blanc fixe	44.47	44.47	44.47
	Add items 10, 11 & 12. Mix at medium speed (1000rpm) for 15 minutes.			
	10 Genable® dispersion addition	0	5	10
	11 Epoxy resin (EEW=250g/eq.)	14.17	9.67	3
	12 Xylene	7.84	7.84	7.84

Part B: Amine Hardener

Item	Raw Material Name	Weight %	Weight %	Weight %
13	Amine hardener	4.27	4.27	4.27

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

3.2. 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, then 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.

3.3. Test Panel Preparation




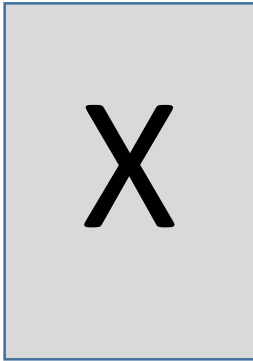

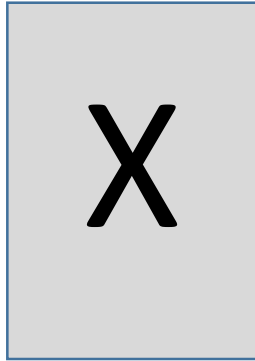
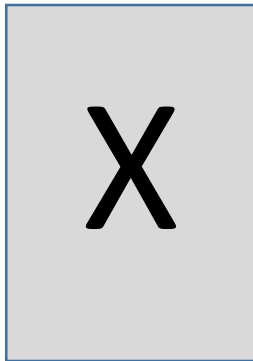

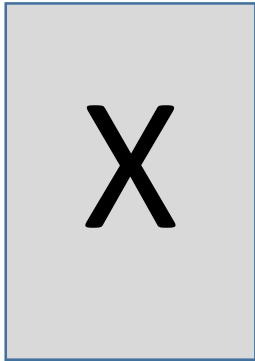
Substrate	Cold rolled steel
Dimensions	152mm by 101mm
Preparation	Grit blasting to SA2-1/2 rolled by degreasing with acetone
Grit	Irregularly shaped chrome/nickel shot
Application	Spray application (gravity-fed gun 1.2mm tip)
Coating Thickness	DFT 60-75 µm
Curing	7 days at room temperature

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


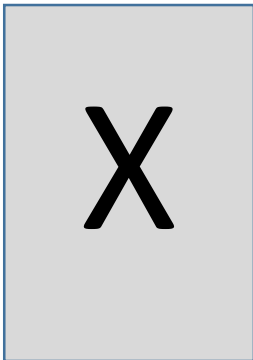
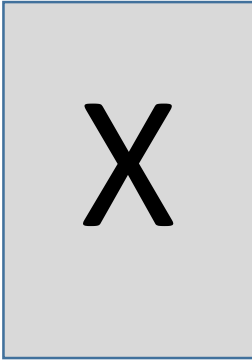
Primer Control **Genable® 1001** and **Genable® 1201** test panels after 1000, 2000 & 3000 hours of testing to ASTM G-85-94:

	Control (Primer Only)	Control + Genable® 1001	Control + Genable® 1201
1000 Hours			
2000 Hours			
3000 Hours			

Primer Control, **Genable® 1001** and **Genable® 1201** test panels (all incorporating 4% wt zinc phosphate) after 1000, 2000 and 3000 hours of testing to ASTM G-85-94:

	4% Zinc Phosphate (Control)	4% Zinc Phosphate + Genable® 1001	4% Zinc Phosphate + Genable® 1201
1000 Hours			
2000 Hours			
3000 Hours			

Primer Control, **Genable® 1001** and **Genable® 1201** test panels (all incorporating 8% wt zinc phosphate) after 1000, 2000 and 3000 hours of testing to ASTM G-85-94:

	8% Zinc Phosphate (Control)	8% Zinc Phosphate + Genable® 1001	8% Zinc Phosphate + Genable® 1201
1000 Hours			
2000 Hours			
3000 Hours			

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

1000 Hours Corrosion Rating Test Results

Primary Anti-Corrosive	Genable® Addition Level in Wet Primer	Graphene in Wet Primer	1000 Hours				Comments
			Creep (mm)	Blistering (Qty)	Size (ISO)	Corrosion	
None	None (Control)	0	>10	0	S0	Ri5	Very poor
None	Genable® 1001 at 5%	0.50%	>10	0	S4	Ri5	Corroded across whole face
None	Genable® 1201 at 10%	0.10%	3	0	S0	Ri3	Corrosion spotting across face
8% ZnPO ₄	None (Control)	0	4	1	S3	Ri5	Corrosion across face
8% ZnPO ₄	Genable® 1001 at 5%	0.50%	2	0	S0	Ri1	Corrosion spotting across face
8% ZnPO ₄	Genable® 1201 at 10%	0.10%	2	0	S0	Ri2	Corrosion spotting across face
4% ZnPO ₄	None (Control)	0	8	1	S3	Ri5	Corrosion across face
4% ZnPO ₄	Genable® 1001 at 5%	0.50%	4	0	S0	Ri0	Good
4% ZnPO ₄	Genable® 1201 at 10%	0.10%	>10	0	S0	Ri5	Completely corroded

2000 Hours Corrosion Rating Test Results

Primary Anti-Corrosive	Genable® Addition Level in Wet Primer	%Graphene in Wet Primer	2000 Hours				Comments
			Creep (mm)	Blistering (Qty)	Size (ISO)	Corrosion	
None	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
None	Genable® 1001 at 5%	0.50%				Ri5	Failed, didn't reach 2000 hours
None	Genable® 1201 at 10%	0.10%	>10	0	S0	Ri3	Corrosion spotting across face
8% ZnPO ₄	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
8% ZnPO ₄	Genable® 1001 at 5%	0.50%				Ri1	Failed, didn't reach 2000 hours
8% ZnPO ₄	Genable® 1201 at 10%	0.10%	3	0	S0	Ri2	Corrosion across much of face
4% ZnPO ₄	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
4% ZnPO ₄	Genable® 1001 at 5%	0.50%	4	0	S0	Ri0	Good
4% ZnPO ₄	Genable® 1201 at 10%	0.10%				Ri5	Failed, didn't reach 2000 hours

3000 Hours Corrosion Rating Test Results

Primary Anti-Corrosive	Genable® Addition Level in Wet Primer	Graphene in Wet Primer	3000 Hours				Comments
			Creep (mm)	Blistering (Qty)	Size (ISO)	Corrosion	
None	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
None	Genable® 1001 at 5%	0.50%				Ri5	Failed, didn't reach 2000 hours
None	Genable® 1201 at 10%	0.10%				Ri3	Failed, didn't reach 3000 hours
8% ZnPO ₄	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
8% ZnPO ₄	Genable® 1001 at 5%	0.50%				Ri1	Failed, didn't reach 2000 hours
8% ZnPO ₄	Genable® 1201 at 10%	0.10%				Ri2	Failed, didn't reach 3000 hours
4% ZnPO ₄	None (Control)	0				Ri5	Failed, didn't reach 2000 hours
4% ZnPO ₄	Genable® 1001 at 5%	0.50%	4	0	S0	Ri0	Good, some spotting on face
4% ZnPO ₄	Genable® 1201 at 10%	0.10%				Ri5	Failed, didn't reach 2000 hours

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

4.2.1. Adhesion Testing

Primary Anti-Corrosive	Genable® Addition Level in Wet Primer	% Graphene in Wet Primer	Force (MPa)			Comments
			Rating 1	Rating 2	Average	
None	None (Control)	0	2	2.25	2.13	50% Adhesive Failure
None	Genable® 1001 at 5%	0.50%	3	3.5	3.25	100% Cohesive
None	Genable® 1201 at 10%	0.10%	1.5	2	1.75	100% Cohesive
8% ZnPO ₄	None (Control)	0	2	2	2	50% Adhesive Failure
8% ZnPO ₄	Genable® 1001 at 5%	0.50%	1	1	1	100% Cohesive
8% ZnPO ₄	Genable® 1201 at 10%	0.10%	2	0.8	1.4	100% Cohesive
4% ZnPO ₄	None (Control)	0	1.25	1.25	1.25	50% Adhesive Failure
4% ZnPO ₄	Genable® 1001 at 5%	0.50%	1.5	1.9	1.7	5% Adhesive 95% Cohesive
4% ZnPO ₄	Genable® 1201 at 10%	0.10%	1.75	2	1.88	70% Adhesive 30% Cohesive

4.2.2. Conical Mandrel Testing

Primary Anti-Corrosive	Genable® Addition Level in Wet Primer	Graphene in Wet Primer	Cracking	Elongation
None	None (Control)	0	0	<35
None	Genable® 1001 at 5%	0.50%	120	3
None	Genable® 1201 at 10%	0.10%	12	19
8% ZnPO ₄	None (Control)	0	4	21
8% ZnPO ₄	Genable® 1001 at 5%	0.50%	100	5
8% ZnPO ₄	Genable® 1201 at 10%	0.10%	120	3
4% ZnPO ₄	None (Control)	0	4	21
4% ZnPO ₄	Genable® 1001 at 5%	0.50%	0	<35
4% ZnPO ₄	Genable® 1201 at 10%	0.10%	11	19

4.2.3. Impact Testing

Primary Anti-Corrosive	Genable® Type & Addition Level in Wet Primer	Graphene in Wet primer (%)	Cracking begins: Height (cm) 1Kg Weight						
			10	20	30	40	50	60	70
None	None (Control)	0.00							
None	Genable® 1001 at 5%	0.50							
None	Genable® 1201 at 10%	0.10							
8% ZnPO ₄	None (Control)	0.00							
8% ZnPO ₄	Genable® 1001 at 5%	0.50							
8% ZnPO ₄	Genable® 1201 at 10%	0.10							
4% ZnPO ₄	None (Control)	0.00							
4% ZnPO ₄	Genable® 1001 at 5%	0.50							
4% ZnPO ₄	Genable® 1201 at 10%	0.10							

4.2.4. Taber Abrasion Testing

Genable® Addition Level in Wet Primer	Graphene in Wet Primer	100 Cycles, 1Kg Weight, CS-C10 Discs			
		Initial Mass (g)	Final Mass (g)	Mass Loss (g)	Wear Rating
None (Control)	0	67.9412	67.9023	38.9	389
Genable® 1001 at 5%	0.50%	67.4874	67.4414	46	460
Genable® 1201 at 10%	0.10%	66.4083	66.3544	53.9	539
None (Control)	0	66.8564	66.8217	34.7	347
Genable® 1001 at 5%	0.50%	67.3164	67.2630	53.4	534
Genable® 1201 at 10%	0.10%	67.0665	67.0396	26.9	269
None (Control)	0	68.1364	68.1008	35.6	356
Genable® 1001 at 5%	0.50%	67.2025	67.1745	28	280
Genable® 1201 at 10%	0.10%	67.6039	67.5674	36.5	365

5. Technical Comments

5.1. Assessing whether Graphene can Enhance Anti-Corrosion Performance.

The aim of the work described in this technical application note is to evaluate if graphene nanoplatelets 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 additives 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 acts as a barrier resistant to water vapour. Work has also shown it could be added into the primer, intermediate or top coating layer.

The results from the testing demonstrate when **Genable® 1001** and **Genable® 1201** is added to a primer or a primer with reduced levels of zinc phosphate then an increase in anti-corrosion performance can be achieved which could lead to a meaningful extension of life.

5.2. Formulating

The **Genable® 1000** and **Genable® 1200** ranges have been developed through a large in-house test programme to demonstrate that graphene could be introduced into a customer's resin. The starting point formulation outlined above is an example of how the **Genable®** graphene can be dispersed directly into the resin formulation. The **Genable®** graphene dispersions are typically introduced into the formulations at the let-down stage.

5.3. Performance

An ongoing long term series of trials are being conducted by AGM based on the ASTM G-85-94 prohesion method. This is a cyclical salt spray test method which is viewed by many in the industry as being representative of real life environmental conditions that a coating system would see in use.

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.

Introduction of a graphene into an epoxy based coating had a significant impact upon barrier properties and consequently on the anti-corrosion performance of the coating system. Whereas after 1000 hours of cyclical salt spray testing the control panels were noted to have excessive corrosion on their surfaces.

Two of the candidate systems demonstrating very good corrosion resistance are the **Genable® 1001** dispersion based coatings with 4% zinc phosphate and the **Genable® 1201** dispersion. The duration of the test was then extended to 2000 hours. Again both the **Genable® 1001** with 4% wt zinc phosphate and **Genable® 1201** (without zinc phosphate) demonstrated very good corrosion resistance with minimal corrosion at the coating interface surface. The **Genable® 1001** test panel with 4% wt zinc phosphate has continued to demonstrate good corrosion resistance at 3000 hours of testing.

6. Genable® 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).

Genable® 1050 has a 3 month shelf life. If settling has occurred during storage simple mechanical mixing will redisperse graphene sufficiently for testing of samples.

Genable® 1250 has a 6 month shelf life with minimal sedimentation expected.

6.3. Solvents

The **Genable® 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 **Genable® 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.

7. Contact Details

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

Email: info@appliedgraphenematerials.com

Phone: +44(0) 1642 438214

You will follow any instructions and all applicable guidelines, laws, regulations, government agency guidelines and best industry practice regarding the use, transport, security, and disposal of the products. All statements and technical information contained in this data sheet are given in good faith and are based on information believed to be reliable, but their accuracy and completeness are not guaranteed and no representation or warranty (express or implied) is given. Any statements and technical information do not constitute an offer to any person and do not form the basis of any contract. All products are sold subject to Applied Graphene Materials' standard terms and conditions of sale. The user will determine the suitability of the products for their intended use prior to purchase and will assume all risk and liability (to the fullest extent permitted under applicable law) in connection with that purchase and intended use. It is the responsibility of those wishing to sell items made from or using the products to inform other users of the properties of the products and the purposes for which they may be suitable, together with all precautionary measures required in handling those products. The information in this datasheet is under constant review and subject to ongoing modification, however, Applied Graphene Materials shall be under no obligation to notify the user of any modifications made.