MATERIALS PERFORMANCE
CORROSION
INNOVATION OF THE YEAR AWARDS

2019 Award Nomination

Title of Innovation:

Graphene based anti-corrosive system

Nominee(s)

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Category:

Coatings and Linings

Coatings and Linings	Instrumentation
Cathodic Protection	Testing
Materials Design	Integrity Assessment
Chemical Treatment	Other—fill in

Dates of Innovation Development:

(from [February, 2017] to [August, 2018])

Web site:

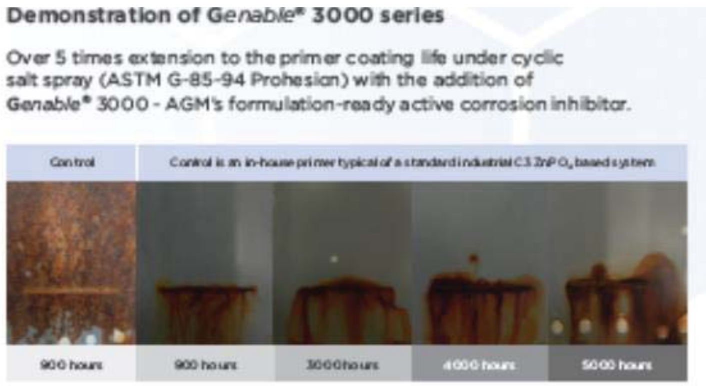
https://www.appliedgraphenematerials.com

Summary Description: G*enable*® 3000 series materials are graphene based active, non-metallic, anti-corrosion additives and have been proven to deliver industry leading performance.

The new series has been formulated to enable the full benefit of graphene materials to be accessed by coatings industry formulators seeking step change anti-corrosion performance, particularly under harsher environmental conditions.

Incorporated into the formulation of an industry standard epoxy primer system, and tested under representative cyclical salt spray testing (ASTM G-85-94 Prohesion), G*enable*® 3000 series materials have demonstrated to deliver a five- fold extension in coating lifetime.

The properties of the **G***enable*® 3000 series make it an ideal tool-box additive for formulators seeking to significantly enhance coating performance in a range of environments. As an additive capable of offering metal-free systems with extended durability it is anticipated that it should find applicability in harsh C4, possibly C5, type environments such as in high humidity industrial, marine and off-shore applications. Once optimised into formulations **G***enable*® 3000 series additives will provide attractive commercial benefits to coating developers and end-users alike, enabling the further optimisation of multi-coat systems and providing significant reductions in application, maintenance and repair costs.



Full Description:

(Please provide complete answers to the questions below. Graphs, charts, and photos can be inserted to support the answers.)

1. What is the innovation?

G*enable®* 3000 series materials are graphene based active, non-metallic, anti-corrosion additives and have been proven to deliver industry-leading performance. The **G***enable®* 3000 series comprise formulated dispersions of graphene nanoplatelets combined with a non-metallic anti-corrosive pigment available in several grades of epoxy. The dispersions solve key problems in utilizing graphene namely; the shop floor handling and management of high aspect ratio 2D materials, easy and effective generation of stable dispersions. Further, the dispersions are formulated to combine graphene with a non-metallic, synergistically active anti-corrosive pigment. This unique combination delivers a significant extension in coating life while permitting non-metallic systems to be used meeting environmental objectives.

2. How does the innovation work?

Protective coatings have essentially three mechanisms; electrochemical, physiochemical as well as being a function of adhesion. The electrochemical behavior of coatings containing active anti-corrosion pigments such as zinc phosphate is well understood in the context of a macroscopic defect such as a scribe introduced during cyclic or continuous salt spray testing. It is typical for the coating technologist to combine mechanisms to achieve the optimum performance of a coating. To be able to combine these individual mechanisms it is important to understand their relationship and the correlation of permeability with anti-corrosive protection has long been recognized. Organic coatings are not impermeable to water and epoxy-based systems, which constitute a major part of today's primer technology, are highly resistant to hydrolysis. Current models of degradation and failure rely on the formation of hydrophilic pathways as a result of hydrolysis and consequent leaching of unreacted materials forming multiple microscopic defects enabling access of water and salts to the metal surface. More recently it has been demonstrated using FTIR and AFM that rapid uptake may occur into free volume and interaction with hydrogen bonding sites adjacent to micro-voids which causes hydroplasticisation and disruption of the polymer network to create hydrophilic pathways through the coating.

Graphene in various chemical and physical forms has been studied to determine whether the material operates by a mechanism, which is based on a passive (barrier) mechanism or also combines an active electrochemical mechanism. It has been reported that graphene based coatings offers excellent short term barrier protection, although once such graphene coatings have been breached, graphene may actually act to electrochemically promote corrosion at the metal interface.

Applied Graphene Materials (AGM) have extensively studied the behavior of graphene nanoplatelets (GNP) in primer systems alone and in combination with active pigments. In the course of this testing AGM have demonstrated that the combination of GNP with a non-metallic active (ion exchange) pigment, a novel “green” anti-corrosive system has exceptional performance. Incorporation of GNP reduces water vapour transmission through a barrier mechanism. EIS evaluation indicated no substantive electrochemical effect over the period measured. Cyclic salt spray, ASTM G85 Annex 5 (prohesion) has indicated significant uplift in corrosion performance compared to a standard primer systems using traditional (zinc phosphate) – up to five times improvement in accelerated salt spray testing.

The mechanism of this synergistic performance uplift is believed to be a hybrid mechanism in which the primary mechanism of the GNP is physiochemical by extending the diffusional pathway creating the so called tortuous path. Acknowledging the models proposed to date for water absorption of undamaged films, it is anticipated that the number of hydrophilic pathways is unlikely to increase on introduction of GNP’s as an additive if the film pigment volume concentration (PVC) remains the same. The synergistic behavior of hybrid system arises from a high efficiency physiochemical barrier effect to water, resulting in a higher degree of controlled and localized hydroplasticisation within the film and a prolonged period of water uptake. The net effect of such a mechanism being the preservation of the active pigment for a longer period resulting in controlled solubilisation of the active component, resulting in enhanced salt spray resistance.

3. Describe the corrosion problem or technological gap that sparked the development of the innovation? How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?

There is significant interest in the development of new anti-corrosion systems which offer a substantial uplift in longevity and performance. Graphene has been demonstrated to provide an exceptional barrier to gas molecules when tested in a single few layer film. The utilization of graphene nanoplatlets provides an opportunity to deliver improved performance in a cost effective manner to existing paint systems, thus avoiding the complexity and practicality of application of graphene as a unique monolayer. **G***enable* 3000 provides a ready and easy to use dispersion in combination with a non-metallic (ion exchange) pigment as a formulating solution applicable to multiple coating formulations. In not containing traditional metal-based pigments the system additionally provides a “green” solution for coating systems.

4. Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation.

G*enable* 3000 has been extensively tested in the laboratory. A basic epoxy coating has been formulated and manufacturing process used is detailed in Part A and B below.

Part A: Epoxy Base

Item	Raw material name	Control (Base Paint plus 8% Zinc Phosphate	Base Paint plus **G***enable*® **3001**
Charge items 1,2,3,4 and 5 and mix at high speed (2000 rpm) for 10 minutes			
		%wt	**%wt**
1	Epoxy Resin (EEW= 250g/eq.)	11.34	11.34
2	Cymel U-216 resin	0.25	0.25
3	Anti-terra U	0.41	0.41
4	Xylene	7.84	7.84
5	Tixogel MP	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
7	Titanium dioxide	11.18	11.18
8	Zinc Phosphate	8	0
9	Blanc Fixe	37.47	43.47
Add items 11, 12 & 13. Mix at medium speed (1000rpm) for 15 minutes.			
10	**G***enable*® 3001 dispersion addition	0	11
11	Epoxy Resin (EEW=250g/eq.)	14.28	4.27
12	Xylene	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. In this case an aliphatic amine hardener was used (e.g. Ancamine 2324).

PVC	35	37
VOC (g/l)	320	309

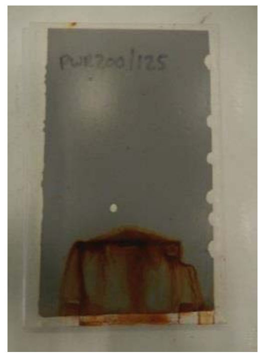
Coatings were applied to mild steel panels measuring 150mm x 100mm x 2mm (5.9in x 3.9in x 0.08in). Panel preparation was by Grit blasting to SA2-1⁄2, using irregularly shaped chrome/nickel steel shot followed by degreasing with acetone. Coating application was by a conventional spray gun using a 1.2mm (0.05in) tip to a dry film thickness of 60-75 microns (3mil) +/-20 microns (0.7mil). The panels were prepared in duplicate for each of the tests to be carried out. The panels were placed in a corrosion chamber, running ASTM G85 annex 5 (prohesion) for a period of up to 5000 hours. Duplicate panels were prepared for assessment at intervals of 500, 1000, 2000, 3000, and 5000 hours, meaning that 10 in total were assessed during the test. The panels were assessed for creep from scribe, blistering, and general appearance using methods: ISO4628-3 Corrosion, ISO4628-2 creep and ISO4628-8 blistering.

Mechanical Testing

Each of the coated samples were subjected to basic mechanical tests including: Taber Abrasion, Conical Mandrel (Elongation ASTM D522), Impact, and Adhesion. Abrasion resistance was carried out using a Taber Abrasion machine, running cycles of 2500 revolutions with abrasive wheels. Each sample was weighed using a precision balance, and the mass loss after each test was calculated. Impact testing was carried out using a 1kg weight dropped from a height of 1m, and assessed for cracking using method: ASTM D2794 - 93(2004). Adhesion was carried out by fixing stainless steel adhesion dollies to the coating sample using a two-component epoxy adhesive. Samples were cured for a period of 7 days, the dollies were removed using a precision adhesion tester giving a measurement of the force required to remove in mega Pascals (MPa), and an indication of the mechanism of coating failure whether it be adhesive of cohesive.

Prohesion testing (ASTMG85 annex 5)

	Control (Primer Only) with 8% Zinc Phosphate	**Control + G*enable*® 3001**
1000 Hours		

2000 Hours	X	
3000 hours	X	
4000 hours	X	

5000 hours	X	

Corrosion Rating Test Results (1000, 2000, 3000, 4000 & 5000 Hours)

Anti-Corrosion Pigment (wt/wt)	Prohesion salt spray exposure (hours)	Creep (mm)	Blistering (Qty)	Blister Size	Corrosion	Comments
Zinc Phosphate at 8%	1000	4	1	S3	Ri5	Failed, Corroded across whole face
G*enable*® 3001 at 11%	1000	1	0	S0	Ri2	Good
G*enable*® 3001 at 11%	2000	1	0	S0	Ri2	Good
G*enable*® 3001 at 11%	3000	1	0	S0	Ri2	Good
G*enable*® 3001 at 11%	4000	1	0	S0	Ri2	Good
G*enable*® 3001 at 11%	5000	1	0	S0	Ri2	Good

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

Adhesion Testing

	Force (MPa)			Comment
Primary Anti-Corrosive	**Rating 1**	**Rating 2**	**Average**	
Zinc Phosphate at 8%	2	2	2	50% Adhesive failure
G*enable*® 3001 at 11%	1.5	1.8	1.65	Cohesive failure

Conical Mandrel Testing

Primary Anti-Corrosive	Cracking	Elongation
Zinc Phosphate at 8%	4	21
G*enable*® 3001 at 11%	0	<35

Impact Testing

Primary Anti-Corrosive	Cracking begins: Height (cm) 1Kg Weight						
	10	20	30	40	50	60	70
Zinc Phosphate at 8%	X	X					
G*enable*® 3001 at 11%	X						

Taber Abrasion Testing

Primary Anti-Corrosive	100 Cycles, 1Kg Weight, CS-10 Discs			
	Initial Mass (g)	Final Mass (g)	Mass Loss (mg)	Wear Rating
Zinc Phosphate at 8%	68.1826	68.1543	28.3	283
G*enable*® 3001 at 11%	67.3551	67.3154	39.7	397

The **G***enable* 3000 system is currently undergoing further in-house evaluation to extend the application envelope to more aggressive environments (C4-C5 ISO 12944). Additionally AGM are seeking to develop water-based equivalents for general application in primer applications. Field trials with GNP modified systems including **G***enable* 3000 are under active exploration with a number of companies.

5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?

G*enable* 3000 can be directly incorporated into paint formulations as demonstrated through the starting point formulation provided. While graphene has historically been seen as an interesting product based on it's barrier performance, there have however been significant issues in the ability of the paint industry to effectively use graphene. This has been due to the difficulties; to disperse graphene, maintain a stable dispersion and handle nano powders with a high aspect ratio. **G***enable* 3000 is a fully stabilized dispersion of GNP with 12 months stability to agglomeration, see table below.

	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

G*enable* 3000 may be incorporated into paint systems using standard production techniques enabling the benefits of graphene to be made available to the coating industry. The combination of the GNP with and active pigment and demonstrated synergistic performance further facilitates it's use. The use of a metal based pigment additionally provides the benefit of a highly efficient "green" anti-corrosion solution which extends service life of assets.

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?

G*enable* 3000 has been commercially available since Q1 2018 and is actively being sampled to customers for trials. The challenges in further development of **G***enable* 3000 lie in (a) the development of further data to support performance claims and (b) the development of systems in matrices other than epoxy and in particular water based chemistries. Current in-house developments are seeking to extend the knowledge base of **G***enable* 3000 in more extreme conditions and the development of new methods to stabilize GNP in water. Further collaboration, either with industry or academics, will accelerate this process. In particular further research to understand in greater detail the precise mechanisms at play and interaction of GNP with different anti-corrosion pigment chemistries will help expand the existing product range and performance.

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.

United Kingdom Patent Application No. 1805856.0

Inventors: W Weaver, L Chikosha, G Johnson, M. Sharp