Graphene/Wax Composites for Improved Anticorrosion

Rich Czarnecki

Micro Powders, Inc.

MICRO POWDERS, INC.
High Performance Wax Additives

Agenda

- Benefits and challenges with nanomaterials
- Chemistry and morphology of graphene oxide
- "Tortuous path" concept for imparting barrier properties
- Novel composite powder for anticorrosion
- Comprehensive powder coating performance data
  - Including salt fog corrosion
- New development for liquid coatings

What is a nanomaterial?

- Most regulatory bodies classify a nanomaterial as:

". . . a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm."

Nanomaterial benefits

- Nano-sized materials can provide properties that are distinctly different from the same material at a non-nano scale
- Nanomaterials can offer unique mechanical, optical and electronic properties

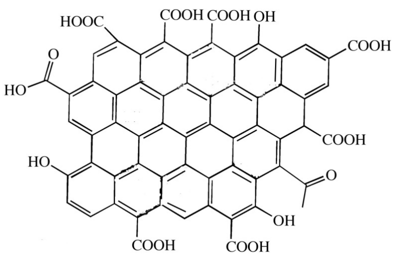
Nanomaterial challenges

- Nanomaterials have an extremely high surface area
  - Very difficult to wet, disperse and homogenize into other materials
- Nanomaterials are fine, dusty powders
  - Difficult to handle, weigh, transfer
  - Plant hygiene considerations

Nanomaterial challenges

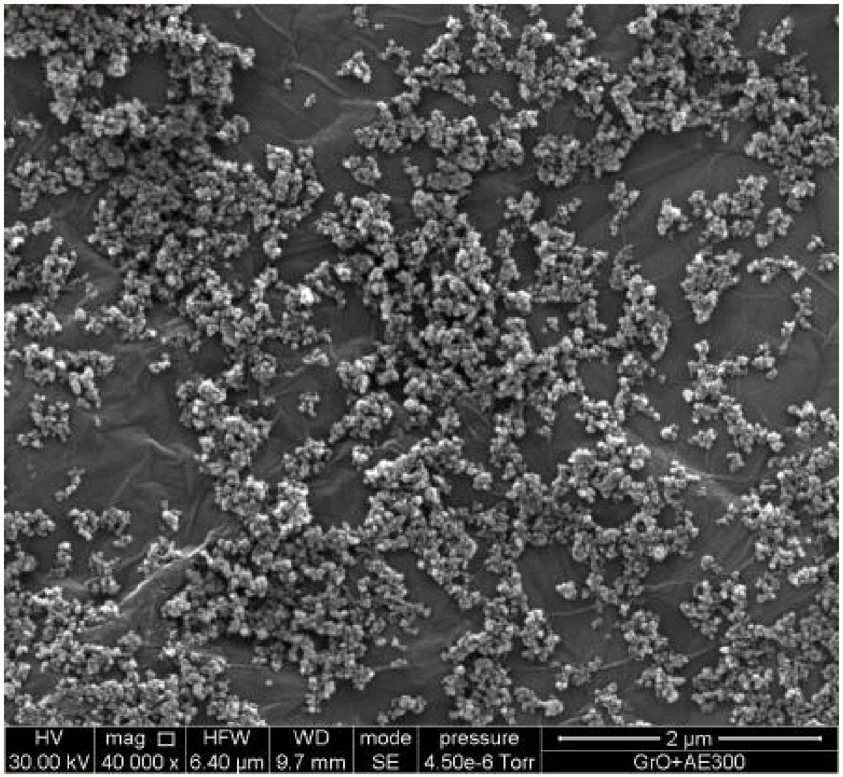
- The health and safety hazards of nanomaterials are not fully understood and continue to be evaluated
- Inhalation hazard studies indicate possible pulmonary effects including inflammation, fibrosis, and possibly carcinogenicity for some materials

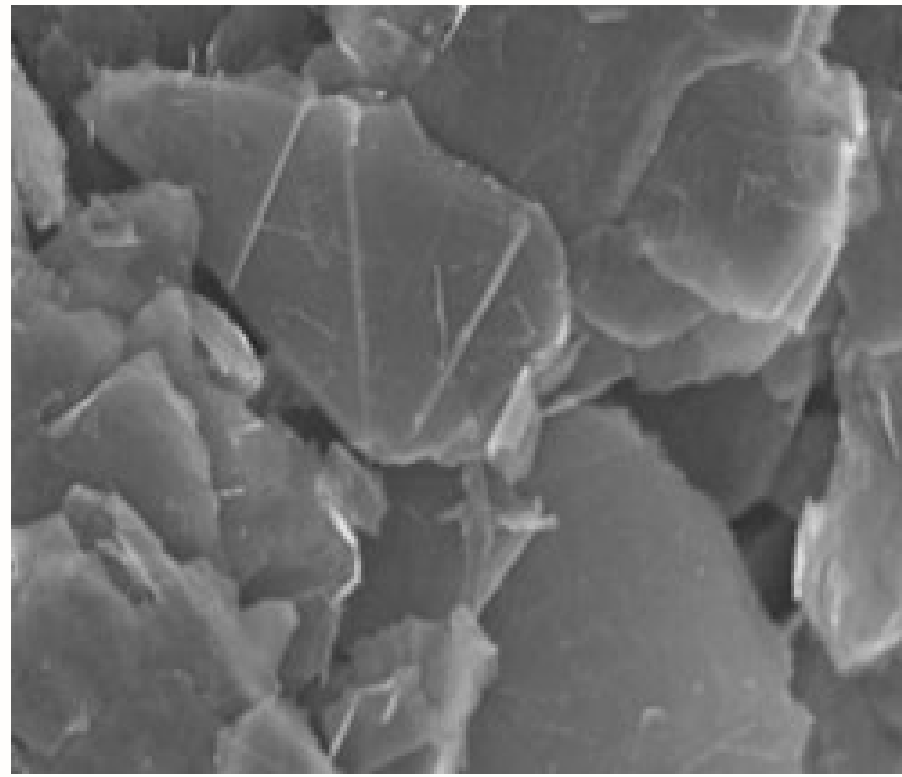
What is graphene?



- A single layer (monolayer) of carbon atoms, tightly bound in a hexagonal honeycomb lattice (high aspect-ratio)
  - the thinnest compound known at one atom thick
  - the lightest material known
  - the strongest compound discovered
    - between 100-300 times stronger than steel
  - the best conductor of heat and electricity
- A high-performance nanomaterial

What is graphene?

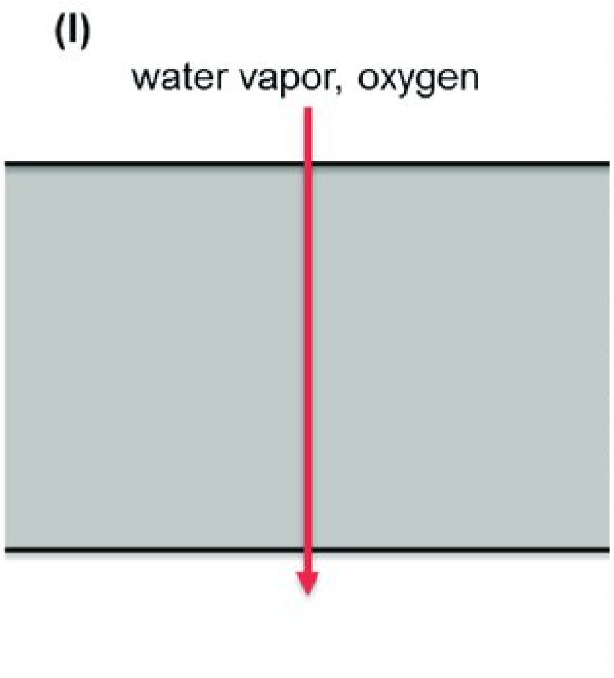




The "Tortuous Pathway" Concept

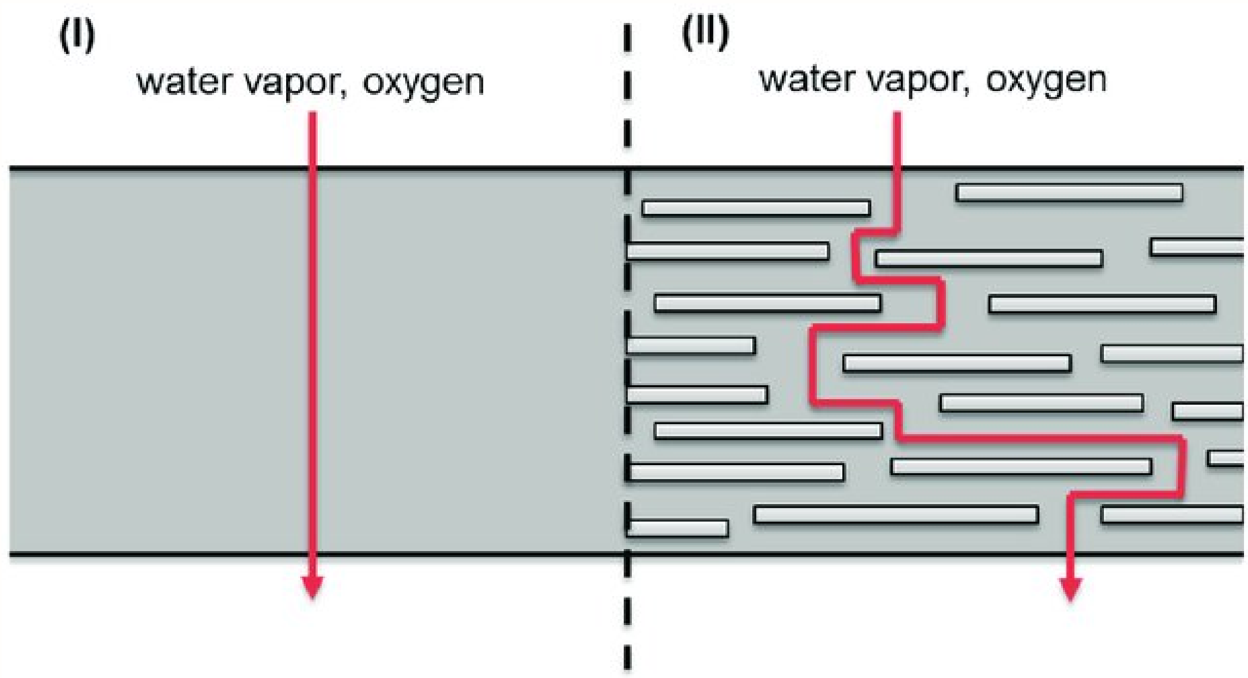
- Physically block and thereby slow the ability of a gas or liquid to migrate through a coating
- Example:
  - Exfoliated clay can be incorporated into extruded plastic films to dramatically improve oxygen barrier properties for food packaging

The "Tortuous Pathway"



Coating cross-section

The "Tortuous Pathway"



Coating cross-section

Partnership with GARMOR

- Micro Powders has partnered exclusively with Garmor (www.garmortech.com) to develop wax additive powders based on Garmor's GO edge-oxidized graphene oxide (EOGO) technology
- Graphene is already known to improve anticorrosion properties by a "tortuous path" mechanism

Graphene nanocomposite

Can we take advantage of the performance of graphene oxide in a form that is easier and safer to use?

- Combine a wax with graphene oxide powder by an extrusion melt/mixing process
- Micronize the resulting nanocomposite material into a typical wax additive particle size

Wax nanocomposites

- Commercially available wax nanocomposite powders deliver high performance nanomaterials in an easy-to-use wax powder
- Aluminum oxide modified wax powders
  - *IMPROVE SCRATCH RESISTANCE*
- Ceramic modified wax powders powders
  - *IMPROVE ABRASION RESISTANCE*

Graphene nanocomposite powder

X-1984 composition:

- A black nanocomposite powder based on synthetic wax and graphene oxide
- Note that synthetic wax is commonly used in powder coatings for antigassing

Properties:

- Melting point 108-113 °C
- Top particle size 31 µm
- Mean particle size 8-12 µm

Objective of this study

- Evaluate overall properties of a powder coating dosed with a graphene oxide/synthetic (Fischer-Tropsch) wax composite (X-1984)
- Study conducted in partnership with The Powder Coatings Research Group (PCRG).

Samples Evaluated

FORMULA	BINDER/CROSS-LINKER	ADDITIVE	ADDITIVE CONCENTRATION	TiO2 –Y OR N?
1	PE/TGIC	NONE	—	Y
2	PE/TGIC	X-1984 graphene nanocomposite	1.0%	Y
3	PE/TGIC	X-1984 graphene nanocomposite	3.0%	Y
4	PE/TGIC	X-1984 graphene nanocomposite	5.0%	Y
5	PE/TGIC	X-1984 graphene nanocomposite	10.0%	Y
6	PE/TGIC	X-1984 graphene nanocomposite	5.0%	N
7	PE/HAA	NONE	—	Y
8	PE/HAA	X-1984 graphene nanocomposite	5.0%	Y

Testing Methods

Weathering Resistance
- ✓ QUV-B Resistance – ASTM D-4589 500 hrs

Corrosion Resistance
- ✓ Salt Fog – ASTM B-117 1250 hrs (or until loss of adhesion/pervasive rust)

Impact Resistance
- ✓ ASTM D-5420

Solvent Resistance
- ✓ ASTM D-5420 (MEK double rubs)

Appearance
- ✓ PCI Smoothness and PCI Texture (using smoothness and texture standards for reference)
- ✓ 60° Gloss

Rheology
- ✓ Pill Flow – ASTM D-4242

Thermal Stability
- ✓ Overbake Resistance – ASTM D-2454 (60° gloss and ΔE/color change)

Effect of X-1984 on Basic Powder Coating Properties

Effect of X-1984 on Basic Powder Coating Properties – Pellet Flow

Wt.% X-1984 Additive	0	1	3	5	10
Pellet Flow (mm)	102	85	54	43	27

- ✓ X-1984 above 1 wt.% significantly retards flow (rheology) of powder paint during cure

Effect of X-1984 on Basic Powder Coating Properties – PCI Smoothness

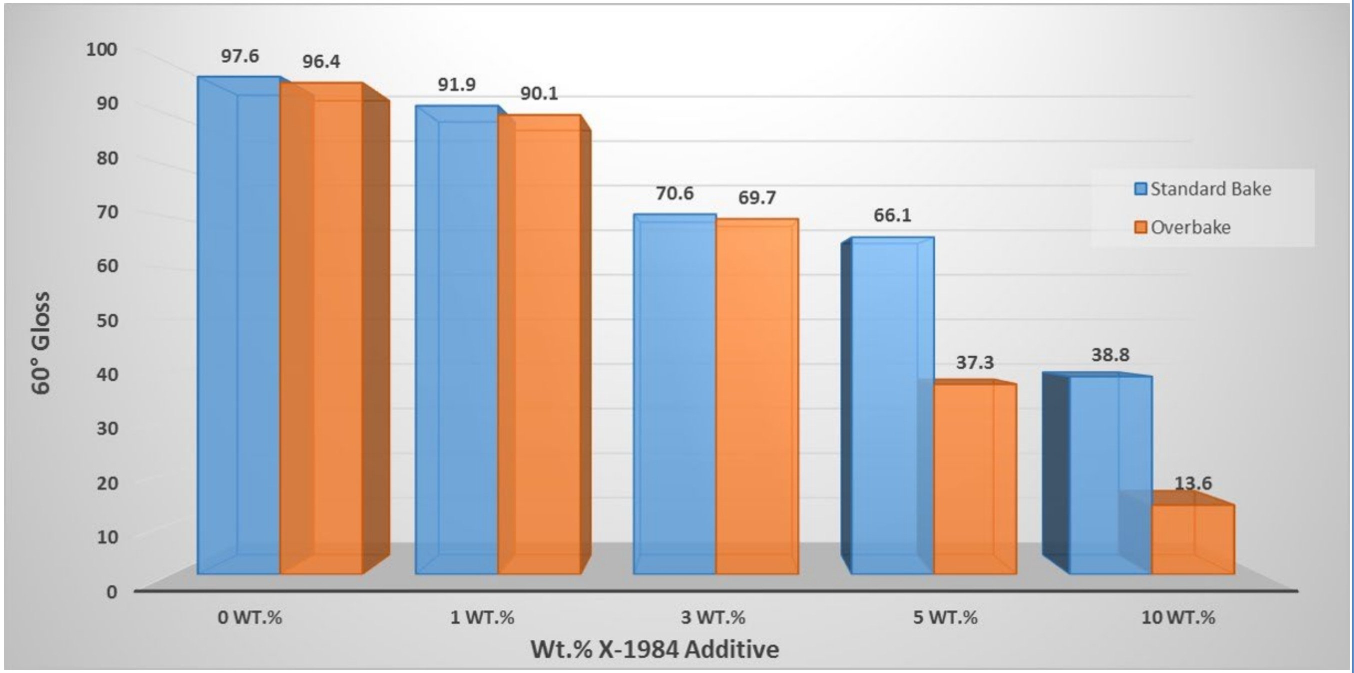
Wt. % X-1984 Additive				
0	1	3	5	10
				
PCI Smoothness Rating				
7	7	7	4	2

- ✓ X-1984 above 3 wt.% significantly affects smoothness of the powder paint coating

Orange peel

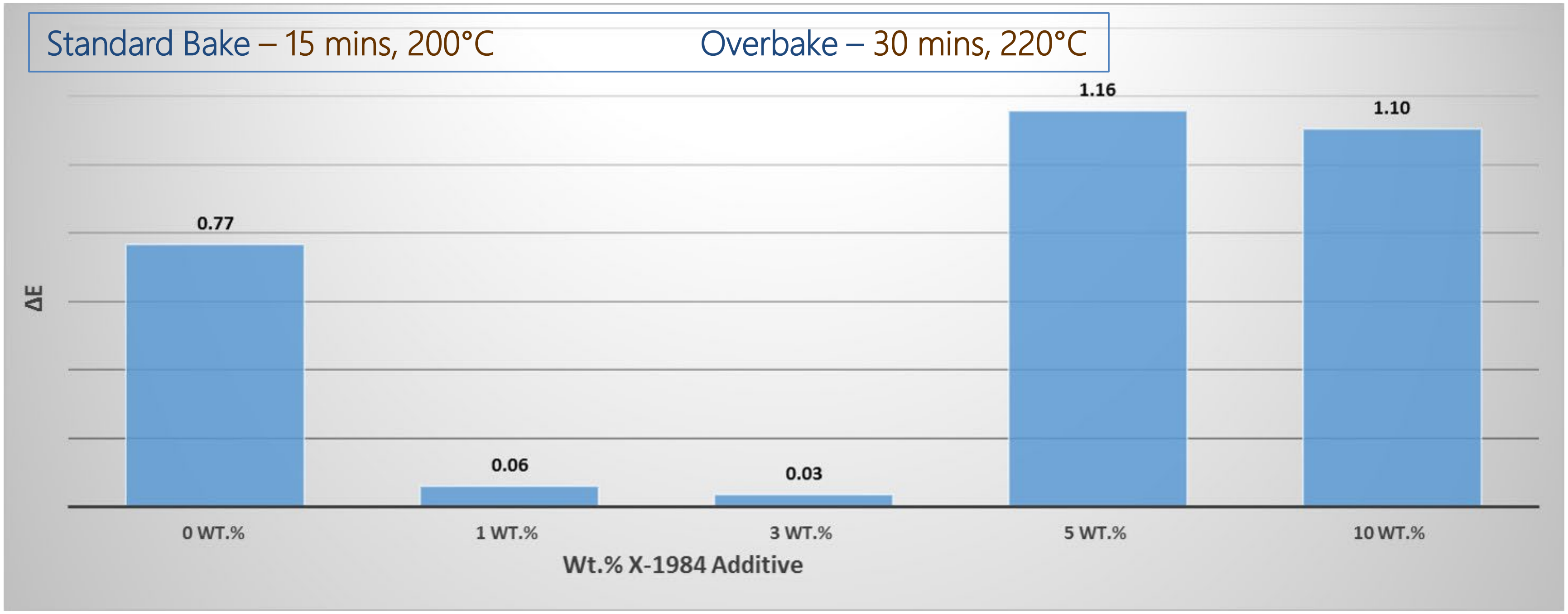
Effect of X-1984 on Basic Powder Coating Properties – 60° Gloss Standard & Overbake

Standard Bake – 15 mins, 200°C   Overbake – 30 mins, 220°C



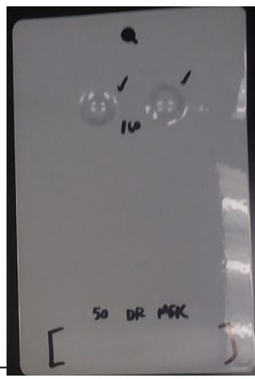
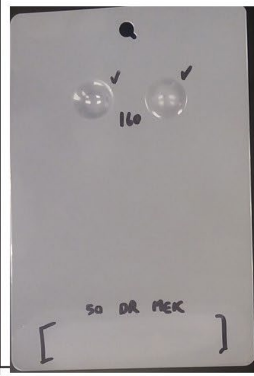
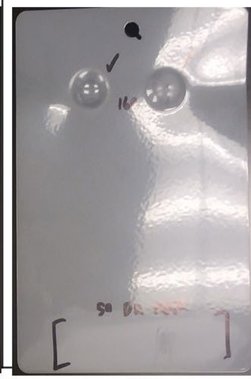
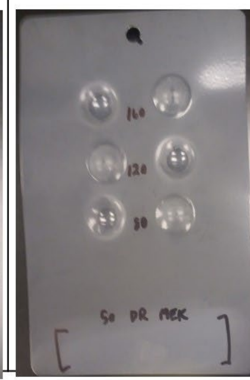
- ✓ As X-1984 concentration increases, the 60° gloss decreases
- ✓ The paint with no additive maintains consistent gloss and addition of 1 and 3 wt.% X-1984 does not adversely affect the thermal stability
- ✓ At and above 5 wt.%, X-1984 is affecting the thermal stability of the coating

Effect of X-1984 on Basic Powder Coating Properties – Color Change (ΔE) Following Overbake



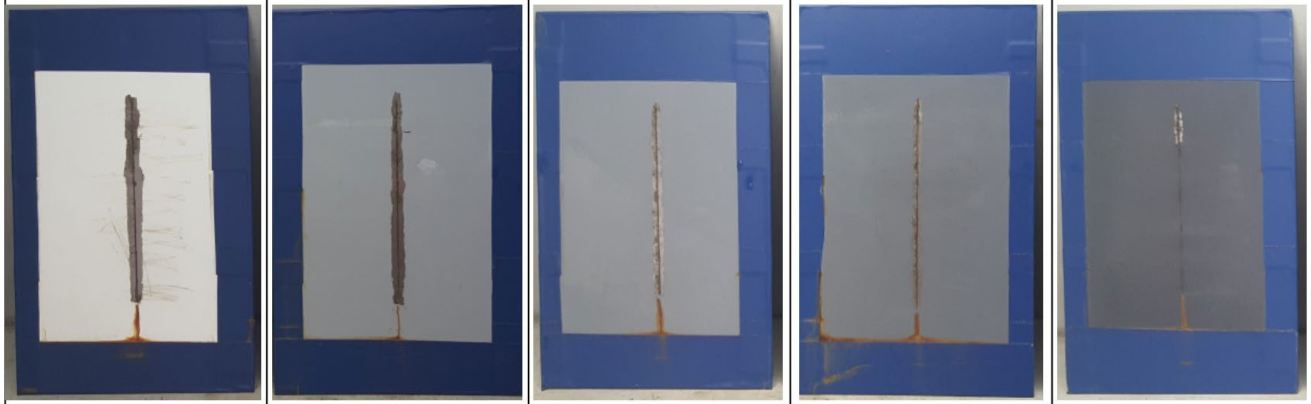
- ✓ Addition of X-1984 increases thermal stability → ΔE decreases at 1 and 3 wt.% levels
- ✓ Consistent with 60° gloss data, addition of X-1984 at and above 5 wt.% decreases the thermal stability of the coating

Effect of X-1984 on Basic Powder Coating Properties – Impact & Solvent Resistance

Wt. % X-1984 Additive				
0	**1**	**3**	**5**	**10**
				
Impact Resistance (in-lb)				
Direct >160 **Reverse** >160	**Direct** >160 **Reverse** >160	**Direct** >160 **Reverse** >160	**Direct** >160 **Reverse** >160	**Direct** 80 **Reverse** 80
Solvent Resistance (50 Double Rubs MEK)				
Softening	Softening	Slight Transfer	Slight Transfer	Transfer

- ✓ The coating *maintains excellent impact resistance at* up to 5 wt.% X-1984
- ✓ The impact resistance significantly decreases with the addition of 10 wt.% X-1984
- ✓ Compared to the control, the solvent resistance decreases only slightly when the X-1984 concentration is ≤5 wt.%; however, 10 wt.% X-1984 has a more negative effect on solvent resistance

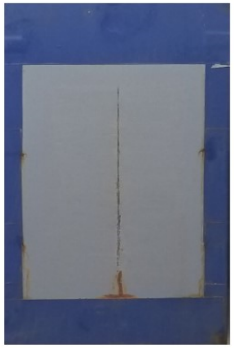
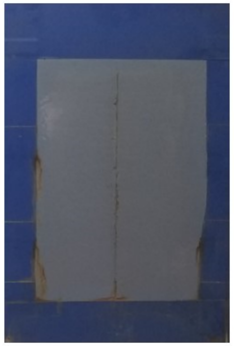
Effect of X-1984 on Basic Powder Coating Properties – Salt Fog Resistance/250 Hrs on Bare CRS

Wt. % X-1984 Additive				
0	**1**	**3**	**5**	**10**
				
Average Creep (mm) on Bare CRS Powder Coated Panels After 250 Hours Exposure to Salt Fog				
2.6	2.0	2.0	1.4	0.4

- ✓ Addition of 1 wt.% X-1984 *decreases the mm creep by ~23%* as compared to the control *after 250 hrs exposure*
- ✓ The *mm creep decreases* ~46% upon addition of 5 wt.% X-1984 *after 250 hrs exposure*

MICRO POWDERS, INC.
High Performance Wax Additives

Effect of X-1984 on Basic Powder Coating Properties – Salt Fog Resistance/1250 Hrs on $FePO_4$ Treated CRS

Wt. % X-1984 Additive				
0	**1**	**3**	**5**	**10**
				
Average Creep (mm) on Fe_3PO_4 Treated CRS Powder Coated Panels After 1250 Hours Exposure to Salt Fog				
0.8	0.6	0.4	0.6	0.2

- ✓ Coatings on $FePO_4$ pre-treated CRS had the best corrosion resistance – corrosion occurred much more slowly
- ✓ Addition of X-1984 at all dosages decreased the mm creep as compared to the Control (no additive)

Effect of X-1984 on Basic Powder Coating Properties – Overall Conclusions

- ✓ Increasing the concentration of X-1984 can retard the flow of the coating during cure (pellet flow) and can also reduce the smoothness of the coating
- ✓ Increasing the concentration of X-1984 decreases the 60° gloss, and at 5 wt.% and above, the thermal (overbake) stability decreases
  - – However, at low levels – 1 and 3 wt.% - X-1984 actually appears to be increasing the thermal stability (i.e., ΔE compared to coating with no additive)

Effect of X-1984 on Basic Powder Coating Properties – Overall Conclusions

- ✓ The coating maintains excellent impact resistance and good solvent resistance when up to 5 wt.% additive is present in coating
  - – However, both the impact and solvent resistance decrease significantly at 10 wt.% additive

- ✓ On bare CRS, the coating with 1 wt.% additive had the best corrosion resistance after 1000 hrs Salt Fog exposure and a slower rate of corrosion

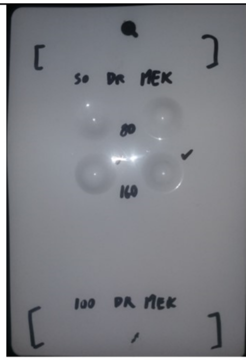
Effect of X-1984 on Basic Powder Coating Properties – Overall Conclusions

- ✓ On $FePO_4$ treated CRS, the coating with 10 wt.% additive had the slowest rate of corrosion and best corrosion resistance after 1250 hrs Salt Fog exposure

- ✓ Increasing the additive concentration increased the weatherability (QUV-B resistance) of the coating

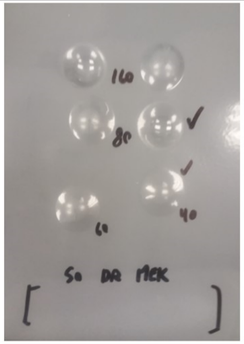
Effect of Cross-linker Chemistry on the Overall Properties of the Powder Coatings

Effect of Cross-linker Chemistry on the Overall Properties of the Powder Coatings

No Additive	
TGIC Cross-linker	**HAA Cross-linker**
	
Impact Resistance (in-lb)	
Direct >160 **Reverse** >160	**Direct** >160 **Reverse** >160
Solvent Resistance (50 Double Rubs MEK)	
Softening	Softening
PCI Smoothness Rating	
7	3
Pellet Flow (mm)	
102	59
60° Gloss (Standard Bake/Overbake)	
97.6/96.4	96.5/92.8
ΔE (Standard Bake vs. Overbake)	
0.77	4.23

- ✓ Changing the cross-linker (i.e., TGIC vs. HAA) in the coating has no effect on impact and solvent resistance
- ✓ The coating containing HAA has a shorter pellet flow and has more orange peel than the coating containing TGIC
- ✓ The coating containing HAA has significantly less overbake stability than the coating containing TGIC

Effect of Cross-linker Chemistry on the Overall Properties of the Powder Coatings

5 Wt.% X-1984 Additive	
TGIC Cross-linker	HAA Cross-linker
	
Impact Resistance (in-lb)	
Direct >160 **Reverse** >160	**Direct** 80 **Reverse** 40
Solvent Resistance (50 Double Rubs MEK)	
Slight Transfer	Slight Transfer
PCI Smoothness Rating	
4	2
Pellet Flow (mm)	
43	45
60° Gloss (Standard Bake/Overbake)	
66.1/37.3	57.2/70.5
ΔE (Standard Bake vs. Overbake)	
1.16	1.94

- ✓ At 5 wt.%, X-1984 significantly decreases the impact resistance of the HAA coating
- ✓ At 5 wt.%, X-1984 increases the orange peel in both coatings – but has the greatest negative effect on the TGIC coating
- ✓ 60° gloss decreases in the TGIC coating with 5 wt.% X-1984
- ✓ 60° gloss of HAA coating increases after overbake
- ✓ The thermal stability of the coating containing HAA improves significantly upon addition of 5 wt.% X-1984

Effect of Cross-linker Chemistry on the Overall Properties of the Powder Coatings – Overall Conclusions

- ✓ Without any additive, the HAA coating has significantly more orange peel than the TGIC coating
  - 5 wt.% of the additive increases orange peel in both HAA and TGIC coatings
- ✓ Without any additive, the TGIC coating has better overbake stability than the HAA coating
  - 5 wt.% of the additive significantly improves the overbake stability of the HAA coating
- ✓ 5 wt.% of the additive significantly decreases the impact resistance of the HAA coating

Effect of Cross-linker Chemistry on the Overall Properties of the Powder Coatings – Overall Conclusions

- ✓ 60° gloss of HAA coating actually increases following overbake – *could be that the additive is fugitive/escapes from coating at higher temperatures/longer bake times?*

- ✓ Corrosion resistance of TGIC coatings was only slightly better than that of the HAA coatings (~17-20 mm creep) both with and without the additive after 750 hrs Salt Fog exposure

- ✓ Addition of the additive resulted in less gloss loss and therefore better weatherability (QUV-B resistance) for both HAA and TGIC coatings (~17% gloss loss for the coatings containing additive and ~25-30% gloss loss for coatings with no additive)

Summary – Corrosion Resistance

- Bare CRS (salt fog resistance; 250 hrs.)
  - 1% **X-1984** decreases the mm creep by **23%**
  - 5% **X-1984** decreases the mm creep by **46%**

- $FePO_4$ treated CRS (salt fog resistance; 1,250 hrs.)
  - 1% **X-1984** decreases the mm creep by **25%**
  - 3% **X-1984** decreases the mm creep by **50%**

X-1984 benefits

- Graphene oxide is already dispersed into a wax particle
  - Easy to process in a powder coating extrusion premix
- No need to wet and disperse the graphene
- Much easier to homogenize graphene into the coating
- Eliminates the hazards of working with nanomaterials
  - Wax composite can be handled like normal wax powder

Other benefits

- Graphene oxide can improve mechanical coating properties
- X-1984 has been found to improve chalking resistance in high temperature powder coatings
- Other improvements in mechanical coating durability can be expected

Future developments

- X-1984 is effective in powder coatings, but what about liquid coating systems?
- X-2260 currently in beta customer testing
- X-2260 is a composite of graphene oxide and a thermoplastic resin that is fully soluble in both alkaline waterbased and solvent based liquid coatings

Conclusions

- Graphene oxide is a powerful additive for improving corrosion resistance in powder coatings
- Improvements in anticorrosion (mm creep) of up to 50% can be achieved
- By incorporating the graphene oxide in a pre-dispersed wax nanocomposite powder, the material is easier and safer to use
- New developments in graphene nanocomposite powders will broaden the use of this technology beyond powder coating systems

Thank You!

Questions?

www.micropowders.com