Examination Of Beneficial Surface Contaminants On Carbon Steel From Select Blast Media

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SHERWIN-WILLIAMS.

Outline

SHERWIN-WILLIAMS.

- Surface Preparation History
- Current Process and Background of Purpose
- Experimental Design
- Results
- Summary
- Future Work

2

History of Surface Preparation

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- **Benjamin Chew Tilghman – inventor of sandblasting in 1870, US patent 108,408**
- **In 1867, D.R. Averill of Ohio patented the first prepared or "ready mixed" paints in the United States**
- **Wheelabrator Tilghman, now known as Wheelabrator Group, was founded in Britain by Tilghman in the late 1800s following his success, and still trades to this day.**
- **First abrasive blasting process was actually a WET blasting process**

3

Surface Cleanliness Standards

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- **ISO 8501 – 1988 combining SIS / DIN – 1967**
- **Purpose…move to an industry standard vs project standards**
  - **40% of the cost of the project is blasting**
  - **Cleanliness = cost**
- **Ultimate performance?**
  - **Not necessarily**

	Brush Off	Industrial	Commercial	Near White	White Metal
Loose Material	None	None	None	None	None
Tight Material	100%	up to 10%	None	None	None
Stains, Shadows	100%	100%	up to 33%	up to 5%	None

4

Background (Phase I)

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- Traditional thought of higher initial dry adhesion will result in longer coating life…all starts with surface preparation
  - 1000, 2000, 5000psi…Is 5000psi better than 1000psi?
  - Highest peak density, highest profile as long as coating covers peak
- Observation of performance differences with different blast media
- Higher performance applications provide differentiation between materials (Oil and Gas Upstream) by more minor surface differences
- What is the difference between abrasive blast media?
- Is the surface of the steel contaminated with material?
- What is the material and what is it doing to the adhesion during performance testing?

5

Background (Phase II)

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- Duplicate learnings from Phase I
  - Material embedded in surface of steel
  - Reliance on profile roughness, peak density, peak height, etc.
- Expand on “Good” and “Bad” contaminant performance in high temperature aqueous immersion service
  - Impact of calcium and sodium ions on blister / adhesion failure
  - Impact of aluminum and magnesium ions on increased performance
- Provide insight into root cause of “Good” ion contaminant benefit
  - Elemental vs oxidized providing electrons available, galvanic series

6

Experimental Design

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Abrasive blast media – (10) Many of the market standards

Linings – (5) Leading epoxy novolacs

Media
Staurolite 1
Nickel slag
Staurolite 2
Fiber slag
Crushed glass
Garnet 1
Garnet 2
Sand
Coal slag
Steel grit

Coating
Coating #1 - Mid
Coating #2 - Mid
Coating #3 - High
Coating #4 - High
Coating #5 - High

Testing
Blast media analysis
SEM / EDX
Steel surface analysis
SEM / EDX
XRD
Optical microscope
Digital microscopy / profilometer
Performance testing
Cathodic disbondment
Isothermal immersions
Atlas cell / Corrocell

Surface *and* Performance analysis…Many, many panels in duplicate

7

Testing Program

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Steel Surface Analysis –

- **Digital Profilometer and Surface Roughness**
- **Surface Energy Contact Angle**
- **Optical Microscopy**
- **SEM / EDX – Surface structure and composition**
- **XRD – X-ray Diffraction to Identify Oxidation State**

Coating Performance Evaluation -

- **Dry Adhesion Evaluation – ASTM D4541 / ISO 4624**
- **Isothermal Immersions – TM 0174**
- **Corrocell / Atlas Cell – ASTM D 6943**
- ***Cathodic Disbondment (TBD)***

8

Surface Analysis

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Sa – Surface Roughness (Deviation from Midpoint)

Coal slag = Highest (28.39)

Staurolite 1 = Lowest (4.51)

Factor = 6.29X

Sensitivity at 0.5 µm

(Testex Tape at 10 µm)

Area	Parameters	Unit	Staurolite 1	Nickel slag	Staurolite 2	Mineral fiber	Crushed glass	Garnet 1	Garnet 2	Sand	Coal slag	Steel grit
10x10 mm2 @100X	Sa	µm	4.51	17.03	7.84	16.64	5.51	10.68	8.26	18.97	28.39	14.35
	Sz	µm	42.25	249.02	103.26	220.45	76.63	216.47	114.71	225.4	318.23	196.94
	Sq	µm	5.62	22.44	9.91	21.01	7.11	14.54	10.41	24.56	36.07	18.33
	Ssk		-0.36	-0.13	-0.35	-0.05	-0.4	-0.31	-0.25	-0.43	-0.14	-0.22
	Sku		3.14	4.56	3.48	3.31	3.96	6.9	3.29	3.92	3.4	3.73
	Sp	µm	17.22	134.61	48.25	102.95	32.48	96.14	51.76	100.57	147.7	96.19
	Sv	µm	25.03	114.41	55.01	117.5	44.15	120.33	62.94	124.83	170.53	100.75

Sa (arithmetical mean height) It expresses, as an absolute value, the difference in height of each point compared to the arithmetical mean of the surface. This parameter is used generally to evaluate surface roughness
Sz (Maximum height) is defined as the sum of the largest peak height value and the largest pit depth value within the defined area.
Sq (Root mean square height) represents the root mean square value of ordinate values within the definition area. It is equivalent to the standard deviation of heights.
Ssk (Skewness) values represent the degree of bias of the roughness shape (asperity).
Sku (Kurtosis) value is a measure of the sharpness of the roughness profile.
Sp (Maximum peak height) is the height of the highest peak within the defined area.
Sv (Maximum pit height) is the absolute value of the height of the largest pit within the defined area.

Surface Structures (100X) – White Metal

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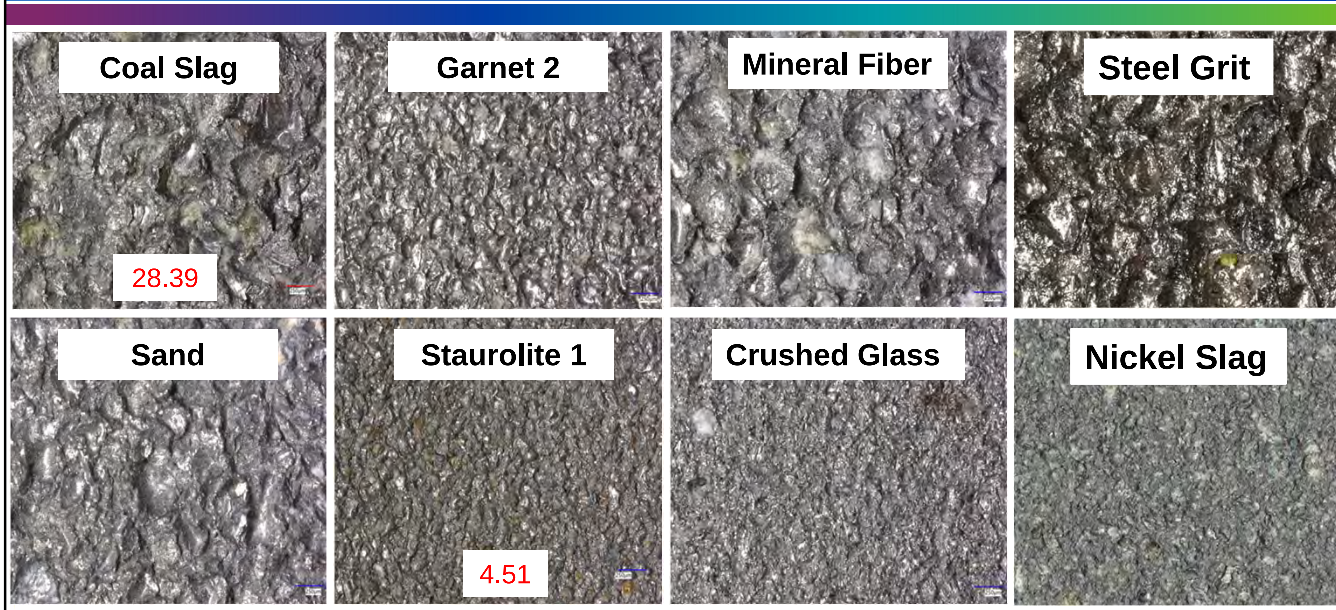

Surface Analysis (Phase I)

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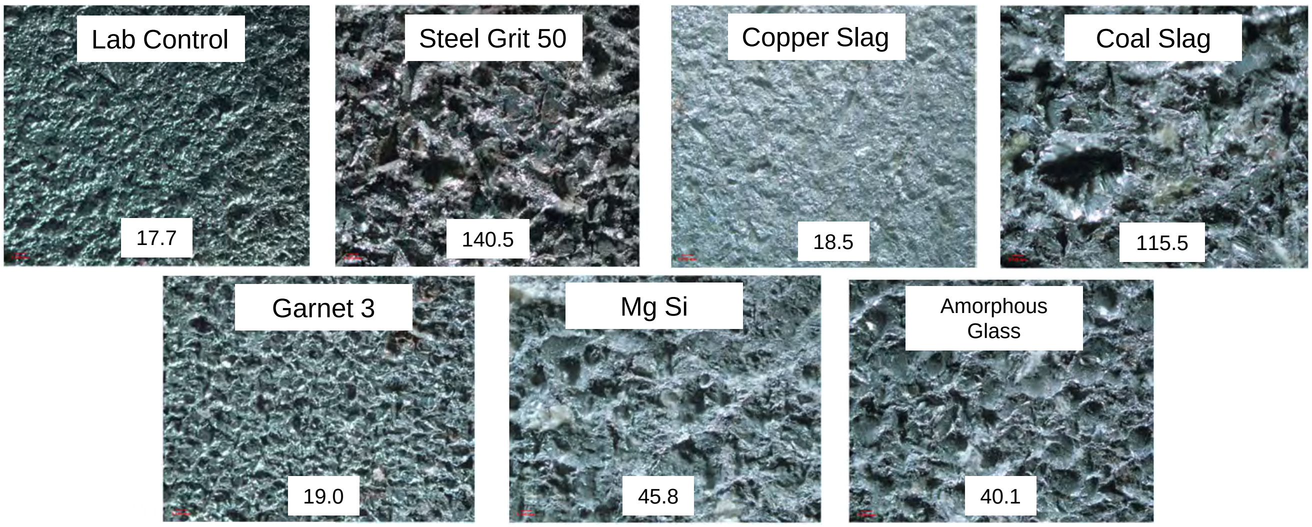
Optical Microscopy – 50X (Deviation Sq in microns)



11

Surface Energy - Goniometer

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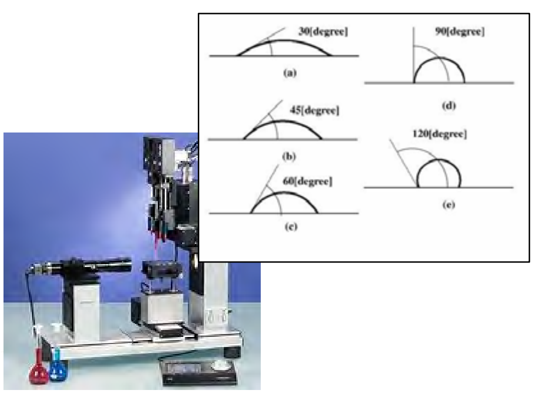
Surface energy after blasting with each media is fairly high and consistent

- Non-factor



Blast Media	Surface Energy (mN/m)
Stautolite 1	71.17
Nickel Slag	78.09
Staurolite 2	60.11
Fiber Slag	71.08
Crushed Glass	71
Garnet 1	High
Garnet 2	70.44
Sand	High
Coal Slag	High
Steel Grit	45.72

12

Surface Analysis

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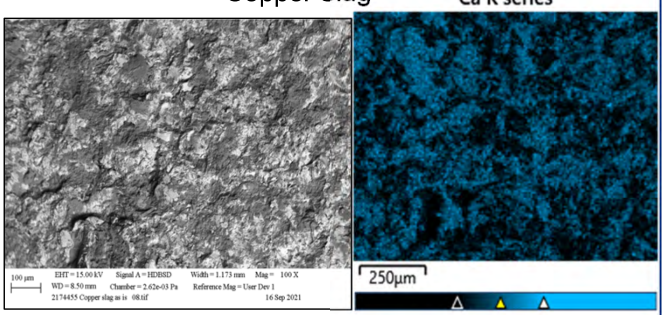
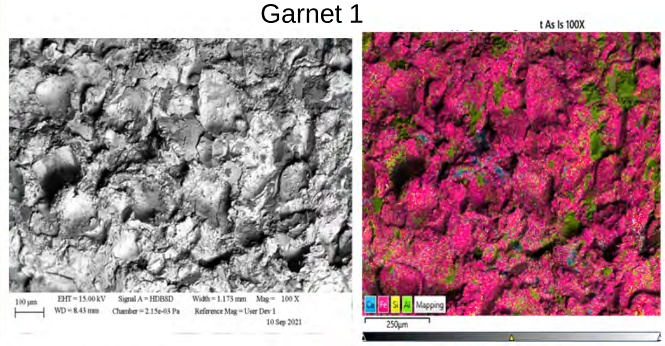
SEM / EDX – Elemental Analysis

Identify where the contaminants are, magnify (SEM), and analyze composition (EDX)

Copper Slag



Garnet 1



13

Surface Contamination (Phase II)

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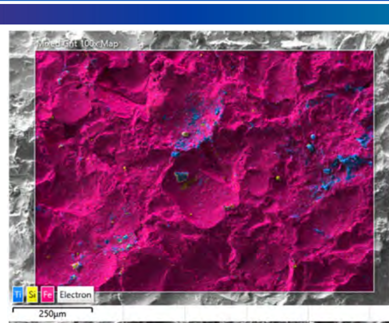
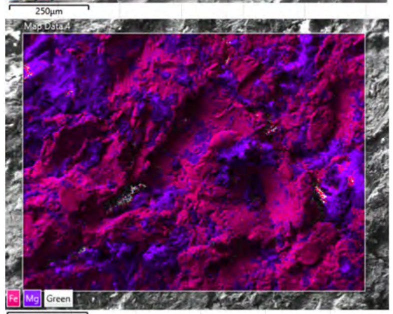
Steel Grit



Nickel Slag



Media	% Fe
Steel grit	84.4
Garnet 2	82.3
Staurolite 2	80.1
Garnet 1	76.3
Sand	72.6
Staurolite 1	69.1
Coal slag	65.7
Crushed glass	65.6
Fiber slag	57.9
Nickel slag	52.3

14

Initial Dry Adhesion (Phase II)

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ALL coatings, **ALL** media = MAX Adhesion (>3500psi)

- Ex. Coatings #1 and #4
- **Profiles are non-factor**
- **Contaminants are non-factor**

Panel position		Left		Right			Left		Right	
Blast media		DFT	Pull off (psi)	DFT	Pull off (psi)		DFT	Pull off (psi)	DFT	Pull off (psi)
Garnet 2		25	3500	27	>3500		21	>3500	25	>3500
Nickel slag		27	>3500	26	>3500		17	>3500	18	>3500
Staurolite 2		23	>3500	21	>3500		21	>3500	21	>3500
Steel grit		21	>3500	16	>3500		2	>3500	22	>3500
Crushed glass		17	>3500	16	>3500		16	>3500	18	>3500
Sand		18	>3500	17	>3500		21	>3500	20	>3500
Coal slag		27	>3500	26	>3500		21	>3500	25	>3500
Fiber slag		21	>3500	16	>3500		14	>3500	21	>3500
Garnet 1		28	>3500	32	>3500		23	>3500	18	>3500
Staurolite 1		16	>3500	14	>3500		24	>3500	20	>3500

15

Surface Analysis - XRF

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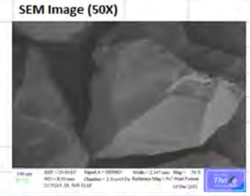
Worst Performance – Crushed Glass

Crushed Glass	Magnification	Si	Na	Ca	O	Low to trace	SEM Image (50X)
	100X	29.9	10.4	6.3	50.6	Al, K, Mg, Fe, Ba, Ti, Mn, S, Cr	
	100X	27.2	9.5	4.5	53.8		
	50X	30.5	9.8	6.7	49.2		
	50X	31.1	9.7	6.9	48.7		
	50X	26.1	9.2	5.6	56.6		
Average		**29.0**	**9.7**	**6.0**	51.8		
STD		2.2	0.4	1.0	2.3		

Crushed glass	Fe	Si	Na	Ca	C	O	Trace (<1%)
Overall (0.8x0.8 mm2) - area with less brown residues	65.6	10.5	4.6	2.2	4.6	11.7	Al, K, Mg, Ti, Mn, Cr
Overall (0.8x0.8 mm2) - area with more brown residues	64.7	10.3	4.6	2.1	4.8	13	
Isolated area	6.1	30.0	8.6	7.3	4.0	42.8	
Isolated area	79.5	4.1	2.3	trace	4.2	8.2	
Isolated area	37.5	20.3	7.1	4.4	4.6	24.5	

16

Surface Analysis - XRF

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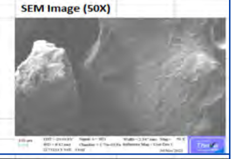
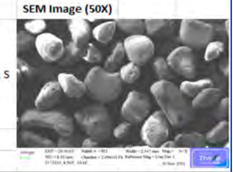
Best Performance –Al / Mg

Staurolite 1	Magnification	Al	Si	Fe	Mg			O	Low to Trace	SEM Image (50X)
	100X	29.3	13.3	15.9	1.1			38.6		
	100X	17.0	15.9	4.8	4.6			55		
	100X	28.2	12.20	9	1			45.8	Na, Ca,Ti, Mn, Zn, P, V, Ni, Ba	
	100X	27	11.90	9.9	0.9			48.9		
	100X	26.6	11.8	9.5	1.0			49.6		
Average		**25.6**	**13.0**	**9.8**	**1.7**			47.6		
STD		4.9	1.7	4.0	1.6			6.8		

Nickel Slag	Magnification	Si	Mg	Fe				O	Low to Trace	SEM Image (50X)
	100X	23.4	20.1	8.6				45		
	100X	23.5	20.5	8.3				45.5		
	50X	21.6	22	4.50				50.5	Al, Cr, Ca, Mn, S, V, Ni, Zn	
	50X	24.0	16.9	7.5				49.2		
	50X	23.5	20.2	8.8				45.2		
Average		**23.2**	**19.9**	**7.5**				47.1		
STD		1.1	2.1	1.9				2.7		



Staurolite 2	Magnification	Al	Si	Fe				O	Low to trace	SEM Image (50X)
	100X	27.9	13.2	10				46.2		
	100X	23.7	16	8.3				50.3		
	100X	24.4	10.7	16.80				45.8	Mg, Ti, Mn, Zn, P, Ba, V, Na, Ca, S	
	300X	26.9	13.3	11.3				45.9		
	300X	26.0	11.9	8.7				50.4		
Average		**25.8**	**12.0**	**12.3**				47.7		
STD		1.3	1.3	4.1				2.2		



Surface Analysis

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Best Performance – Multiple…Staurolites, Nickel Slag, Garnet

Staurolite 1	Fe	Al	Si			C	O	Trace (<1%)
Overall (0.8x0.8 mm2)	69.1	8.0	3.8			3.6	13.2	
Isolatedsmall area	71.3	6.9	3.8			3.6	11.9	Na, Ca,Ti, Mn, Mg
Isolated area	85.1	2.6	1.50			3.2	6.9	
Isolated area	5.2	21.8	9.7			10.2	51.5	

Nickel slag	Fe	Si	Mg			C	O	Trace (<1%)
Overall (0.8x0.8 mm2)	52.3	11.3	8.9			6.6	20.4	Al, Ca, Cr, Mn, Ti
Isolated area	73.8	5.1	5.5			3.9	11.5	
Isolated area	16.8	20.7	11.8			9.8	38.1	
Isolated area	81.2	3.0	3.2			4.8	7.5	

Staurolite 2	Fe	Al	Si	Ti		C	O	Trace (<1%)
Overall (0.8x0.8 mm2)	80.1	3.0	1.3	1.8		5.1	7.7	
Isolated area	83.6	2.0	1.1	1.9		4.2	6.5	Mn, Ca, P, Mg
Isolated area	94.2	trace	trace	trace		1.4	1.8	
Isolated area	61.4	10.3	4.1	1.6		5.5	16.6	

Coating Performance

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Five High Solids Epoxy Novolac Linings

Key Oil and Gas market protective linings

- **Coating #1** - A solvent free, two component polycyclamine cured lining system utilising advanced epoxy novolac technology with flake and fibre reinforcement
- **Coating #2** – A solvent free mid performance epoxy novolac lining with good chemical resistance
- **Coating #3** - A solvent free high performance, PTFE, inert flake reinforced, novolac tank lining
- **Coating #4** – A solvent free high performance epoxy novolac lining with excellent chemical resistance
- **Coating #5** – A solvent free very high performance epoxy novolac lining with increased chemical resistance

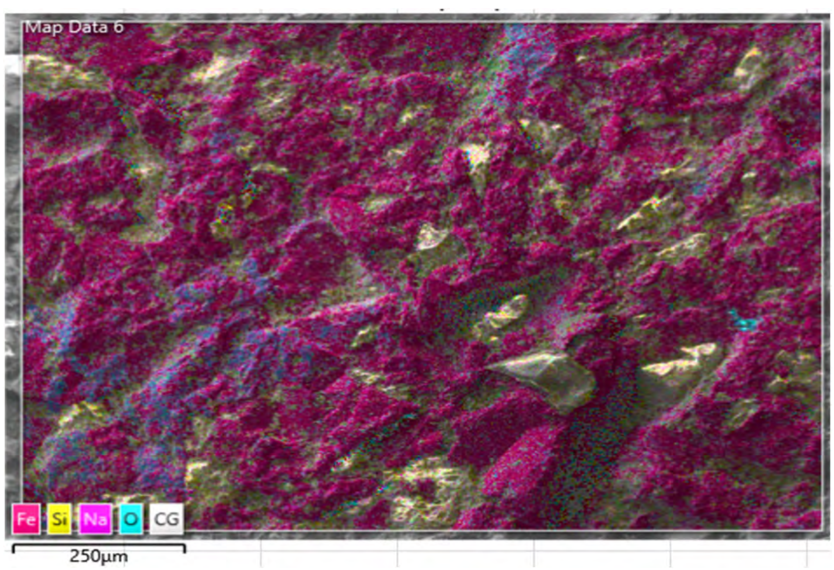
19

Immersion Performance

SHERWIN-WILLIAMS.

Crushed Glass –

Media	% Fe
Staurolite 1	69.1
Nickel slag	52.3
Staurolite 2	80.1
Fiber slag	57.9
Crushed glass	65.6
Garnet 1	76.3
Garnet 2	82.3
Sand	72.6
Coal slag	65.7
Steel grit	84.4



20

Immersion Performance

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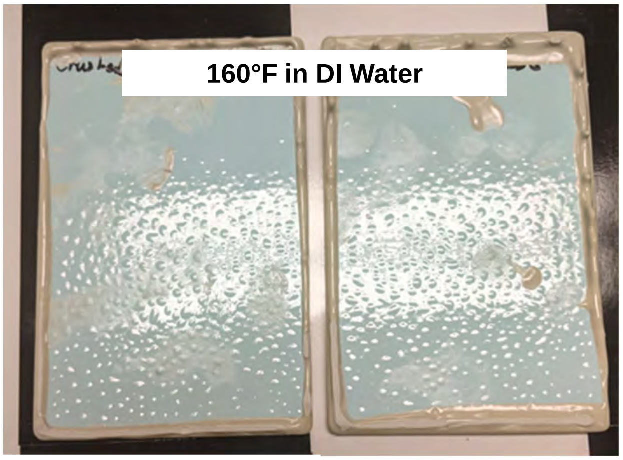
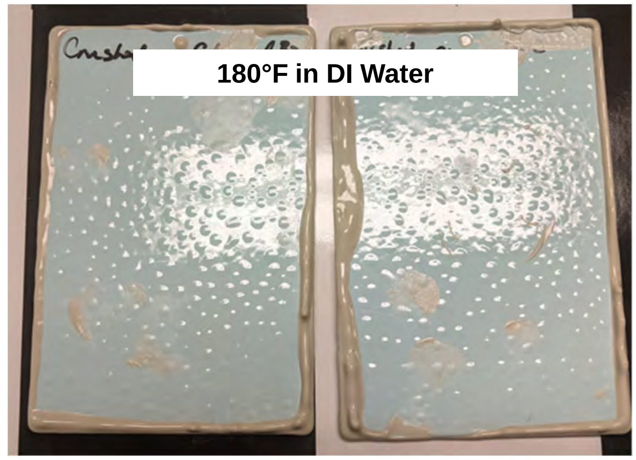
Strong osmotic blisters present with Coating #2 (high performance)



160°F in DI Water



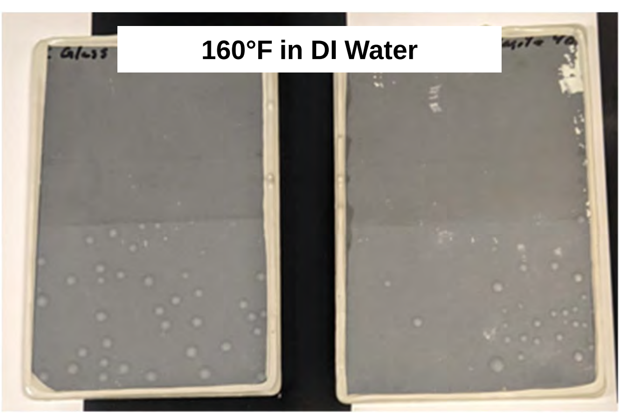
180°F in DI Water

21

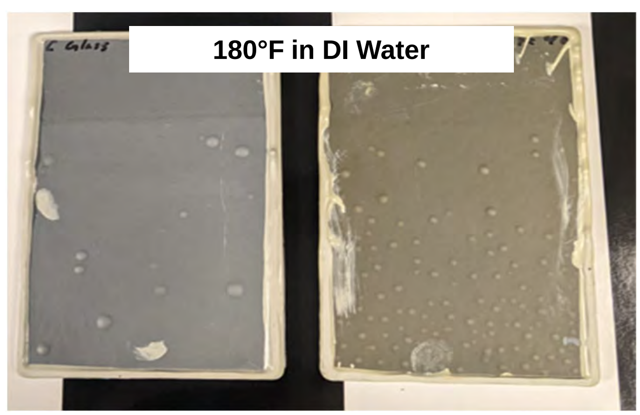
Immersion Performance

SHERWIN-WILLIAMS.

Strong osmotic blisters present with Coating #5 (highest performance)



160°F in DI Water



180°F in DI Water

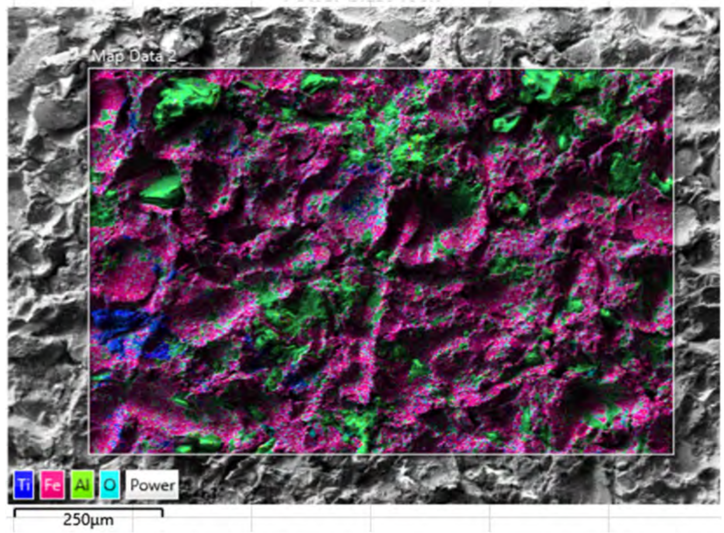
22

Immersion Performance

SHERWIN-WILLIAMS.

Staurolite 1 –

Media	% Fe
Staurolite 1	69.1
Nickel slag	52.3
Staurolite 2	80.1
Fiber slag	57.9
Crushed glass	65.6
Garnet 1	76.3
Garnet 2	82.3
Sand	72.6
Coal slag	65.7
Steel grit	84.4



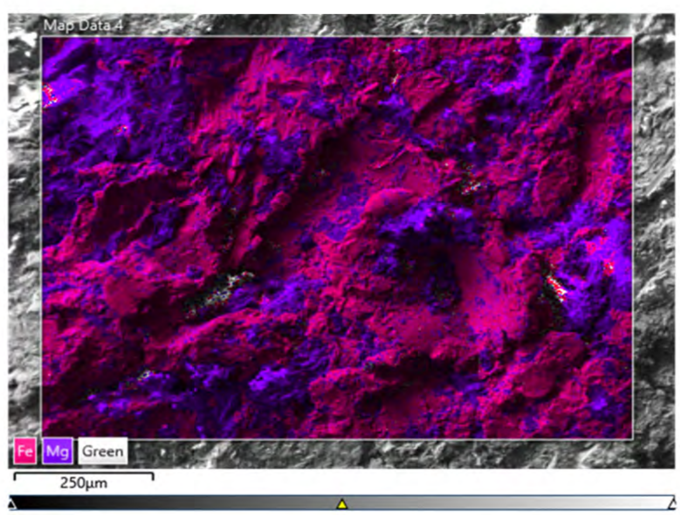
23

Immersion Performance

SHERWIN-WILLIAMS.

Nickel Slag –

Media	% Fe
Staurolite 1	69.1
Nickel slag	52.3
Staurolite 2	80.1
Fiber slag	57.9
Crushed glass	65.6
Garnet 1	76.3
Garnet 2	82.3
Sand	72.6
Coal slag	65.7
Steel grit	84.4



24

Immersion Performance

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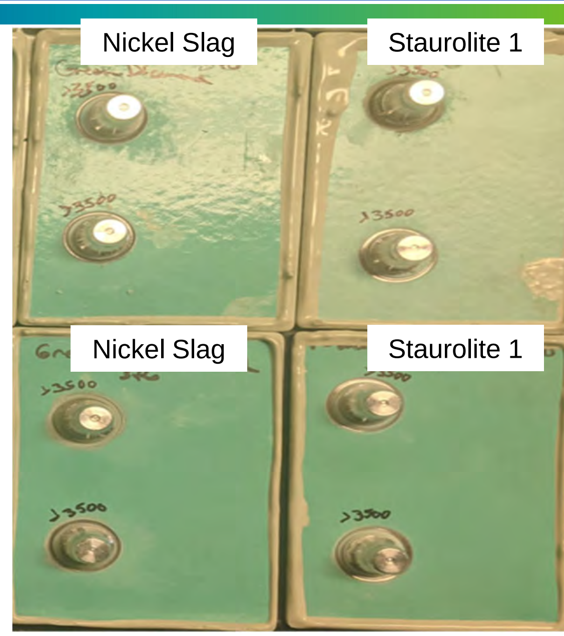
Coating #1 – Medium Performance Epoxy

- **180°F Immersions for 30days**
- **Pull-off adhesion - >3500psi (MAX)**
- **No Blisters**
- **Best results with high levels of Al / Mg**
- **Duplication of Phase I, 2021 results**



25

Immersion Performance

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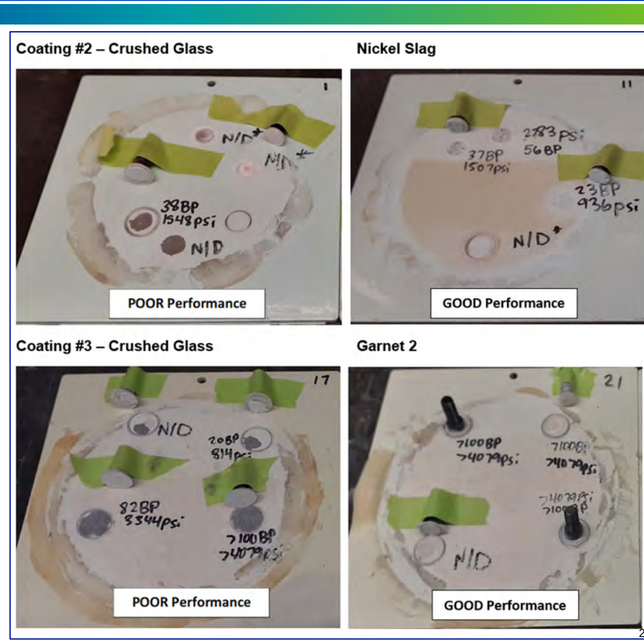
Atlas Cell at 212°F for 1 Month

- **Ca / Na** provide for failure in higher performance Coating #2 and #3
- **Good** performance equals cohesive failure with no blisters
- **High performers = Al / Mg**
  - **Garnet 1**
  - **Garnet 2**
  - **Nickel slag**
  - **Staurolite 1**
  - **Staurolite 2**



26

Coating Performance (Phase I Ref.)

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- High Levels of **Calcium** and **Sodium** caused lower performance
- Higher performance coatings can compensate for contaminants of concern *(#2 and #3)*
- Lower performance coatings are more sensitive to surface cleanliness
- Greater amount of iron oxide formation provides lower performance…**Garnet 4, Steel Grits**
- Some correlation with higher levels of **Magnesium** and increased performance
  - Oxidation state…galvanic protection?

Isothermal Immersion at 180°F for 1 month –

Pass = No blisters in significant surface area

Fail = Less and smaller blisters

Fail = Blisters and loss of adhesion

Blast Media	Condition	Coating #1	Coating #2	Coating #3
Steel Grit 40 M	*N*	Fail	Pass	Pass
	S	Fail	Pass	Pass
Steel Grit 50 M	*N*	Fail	Pass	Pass
	S	Fail	Pass	Pass
Garnet 1	*N*	Pass	Pass	Pass
	S	Pass	Pass	Pass
Garnet 2	*N*	Pass	Pass	Pass
	S	Pass	Pass	Pass
Garnet 3	*N*	Pass	Pass	Pass
	S	Pass	Pass	Pass
Garnet 4	*N*	Fail	Pass	Pass
	S	Fail	Pass	Pass
Coal Slag	*N*	Fail	Pass	Pass
	S	Fail	Pass	Pass
Amorphous Silicate	*N*	Fail	Pass	Pass
	S	Fail	Pass	Pass
Nickel Slag	*N*	Pass	Pass	Pass
	S	Pass	Pass	Pass
Magnesium Silicate	*N*	Pass	Pass	Pass
	S	Pass	Pass	Pass
Steel / Sod Bicarb	*N*	Fail	Fail	Fail
	S	Fail	Fail	Fail
Copper Slag	*N*	Fail	Pass	Pass
	S	Fail	Pass	Pass

27

Surface Analysis (Phase I)

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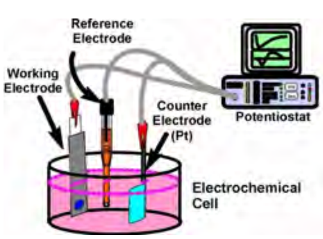
Electrochemistry – Potentiostat direct current (polarization resistance)

- Quick, robust measurement of possible passivation of the steel from contamination such as silicates or alkaline salts.
- Higher iCorr = more **Anodic** reaction…**Oxidation**
- **5% NaCl Used**



The Butler-Volmer Equation is a general electrochemical equation that describes the relationship between the potential and the current (kinetics) in a mixed potential system.

$$I = I_a + I_c = I_{CORR}(e^{(2.3(E-Eoc)/\beta a)} - e^{(-2.3(E-Eoc)/\beta c)})$$

Rate of anodic reaction

Rate of cathodic reaction

Where:
I = cell current (A)
I_{CORR} = corrosion current (A)
E = applied potential (V)
E_{oc} = corrosion potential (V)
β_a = anodic Tafel constant (V/decade)
β_c = cathodic Tafel constant (V/decade)

Blast Media	Icorr
Garnet 3	642.2
Amorphous Silica	643.1
Copper Slag	782.2
Coal Slag	837.4
Garnet 2	1076.0
Magnesium Silicate	1151.2
Garnet 1	1166.5
Nickel Slag	1228.5
Steel Grit 50 Mesh	1237.0
Lab Control	1266.0
Steel Grit 40 Mesh	1397.5
Steel Grit / Sod Bicarb	1455.5
Garnet 4	1844.3
Aluminum panel	*4.3*
Aluminum panel (sanded)	*4.9*

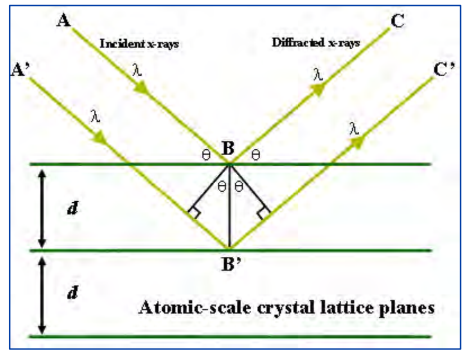
28

XRD – Oxidation State

SHERWIN-WILLIAMS.

X-ray Diffraction – Determine crystal structures and composition

- Ex. A metal silicate with various transition metal oxidation states
- Scans are compared to a database
- Relative composition structures are determined
- Requires an oxidation state…no free electrons
- Galvanic ability is limited

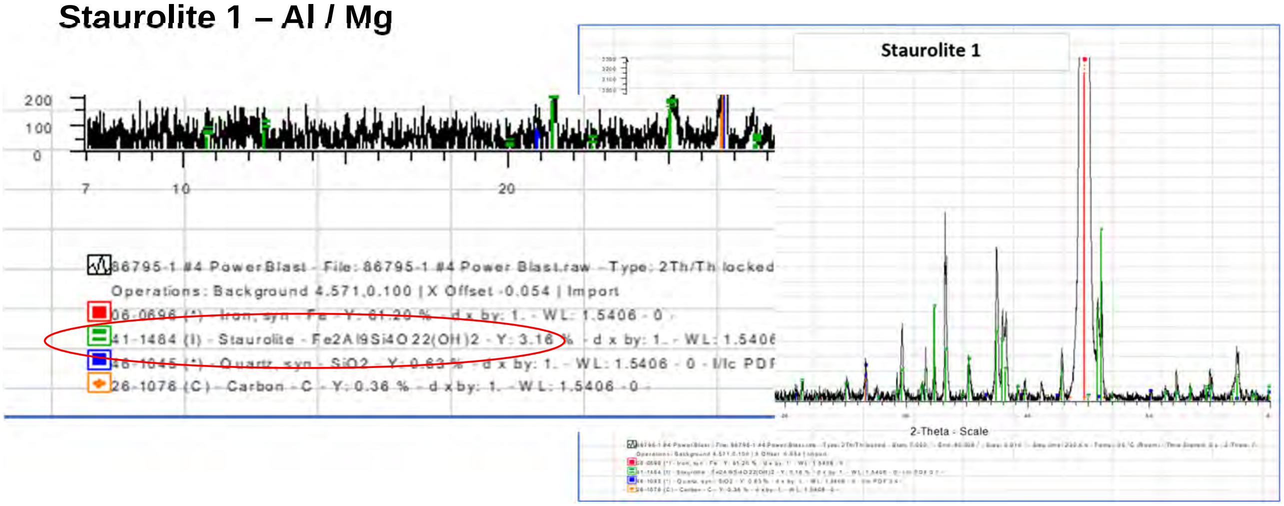


29

XRD – Oxidation State

SHERWIN-WILLIAMS.

Staurolite 1 – Al / Mg



30

Summary

SHERWIN-WILLIAMS.

- Roughness and initial adhesion don't play as much of a factor on performance as contamination and composition…anyway you slice it…
- Different abrasive blasting media leave different levels and composition of contamination on the surface of the steel that are invisible (All SP5) to the eye
- Slight differences between the composition of contaminants have an impact on the performance of the applied coatings
- Calcium and Sodium ions confirmed to provide poor immersion performance
- Magnesium and Aluminum ions confirmed to provide improved performance
- Evolution of higher performance (better chemistry) coatings can overcome much of the contamination
- Should blast media be part of high temperature immersion service specification?

31

Future Testing

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- Utilize electrochemistry measurements to determine benefit and detriment of certain contaminants…try
- Evaluate wet blasting / vapor blasting surface contamination and correlation to work presented here

32

Surface Analysis

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Biggest Concern of Project – Difficult to Control

SWEAT!!!! – August in Houston, TX

33

Thank You!
Questions?

Protective & Marine Coatings