

Coatings formulation against corrosion: Smart use of Nubirox anticorrosive pigments

UL Prospector Webinar

14th February, 2018



Agenda

Anticorrosive pigments:

- What is corrosion? Mechanism of corrosion protection
- Anticorrosive pigments:
 - Historical evolution
 - Nubirox Zinc based and Non Zinc based pigments:
 - Inhibition mechanism
 - Physical properties
 - Pigment surface treatments

Anticorrosive coating formulation:

- Formulation parameters
- Examples of coating formulation:
 - Replacement of conventional Zinc phosphate in a SB Alkyd primer
 - Improving corrosion protection of WB DTM coatings



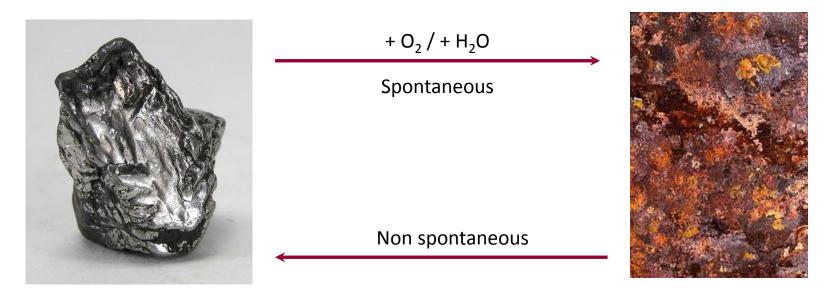




Corrosion

WHAT IS CORROSION?

Corrosion is a gradual **spontaneous** process as a result of a chemical reaction with the environment that damages the original metal



Entropy: Order \rightarrow Disorder



Corrosion

COST OF CORROSION

The annual cost of steel corrosion, estimated to be **\$2.5 trillion globally**, which is equivalent to **3,4%** of the global GDP (2013)

Source: "NACE International assessment of the global cost of corrosion" 2016





Corrosion

HOW DOES CORROSION OCURR?















Corrosion mechanism

Fe → Fe²⁺ + 2e⁻ O_2 + 2 H₂O + 4 e⁻ → 4 OH⁻ Humidity Contaminants Temperature Light



Protection

HOW DO WE SLOW DOWN CORROSION?

Corrosion cannot be 100% avoided, but we can slow the process down.





Protection

HOW DO WE SLOW DOWN CORROSION?

Barrier protection

 Coating: Impermeability of the paint film, film thickness, pigment selection (e.g., type, morphology, size...)

Sacrificial protection

Cathodic protection: Zinc Rich Coatings (Zinc Dust).

Zinc works as sacrificial anode and it is corroded instead of the steel.

Inhibitive protection

- Corrosion inhibitors: Inhibiting the rate of corrosion either chemically and/or electro-chemically (inorganic & organic)
 - Cathodic corrosion inhibitors
 - Anodic corrosion inhibitors
 - pH control



Nubirox anticorrosive pigments



Anticorrosive pigments evolution

TRADITIONAL ANTICORROSIVE PIGMENTS

Chromate based pigments

Zinc Chromate Zinc Tetraoxychromate Strontium Chromate Barium Chromate Red lead

ALTERNATIVE NON CLASSIFIED AS HAZARDOUS ANTICORROSIVE PIGMENTS

ZINC BASED PIGMENTS

• Zinc Phosphate

Nubirox N2 Nubirox SP (special particle)



Modified Zinc Phosphates

Modified with molybdate and organic surface treatment
 Nubirox 102
 Nubirox 106 (special particle)

-Modified with iron phosphate **Nubirox 213** (special particle)

NON ZINC BASED PIGMENTS

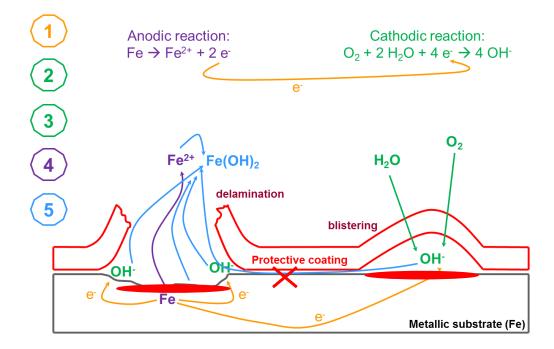
Calcium strontium phosphosilicate

Nubirox 301

Nubirox 302 Modified with organic surface treatment



Anticorrosive pigments mechanism

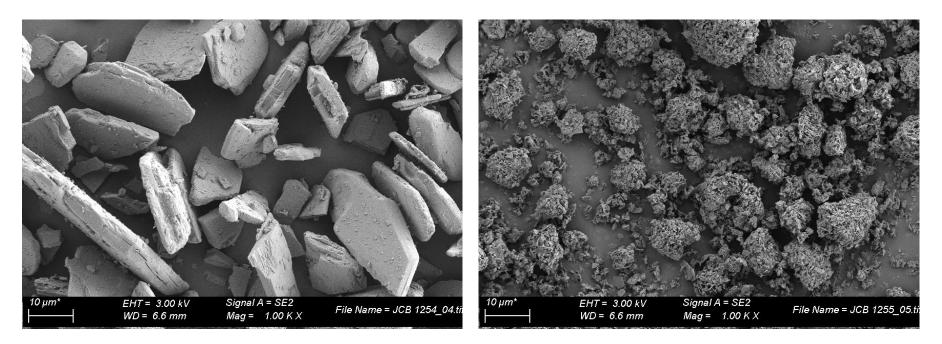


- Zinc phosphate (Nubirox N2, SP, 102, 106 & 213):
 - Direct anodic passivation: Zn phosphate complexes
 - Cathodic inhibition: basic Zn oxides
- Calcium Strontium phosphosilicate (Nubirox 301 & 302):
 - Direct anodic passivation: Ca, Sr, Fe phosphate complexes
 - Cathodic inhibition: basic Ca, Sr oxides



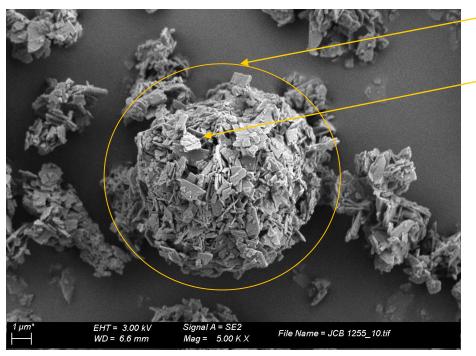
Zinc phosphate: same chemistry but different physics

Conventional Zinc Phosphate Nubirox N2 Special particle Zinc Phosphate Nubirox SP





• Nubirox SP: Special particle Zinc Phosphate

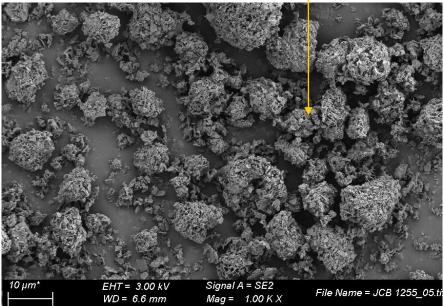


Microscope pictures (SEM)

Aggregated lamellar crystals forming a spherical agglomerate (4-10 μm)

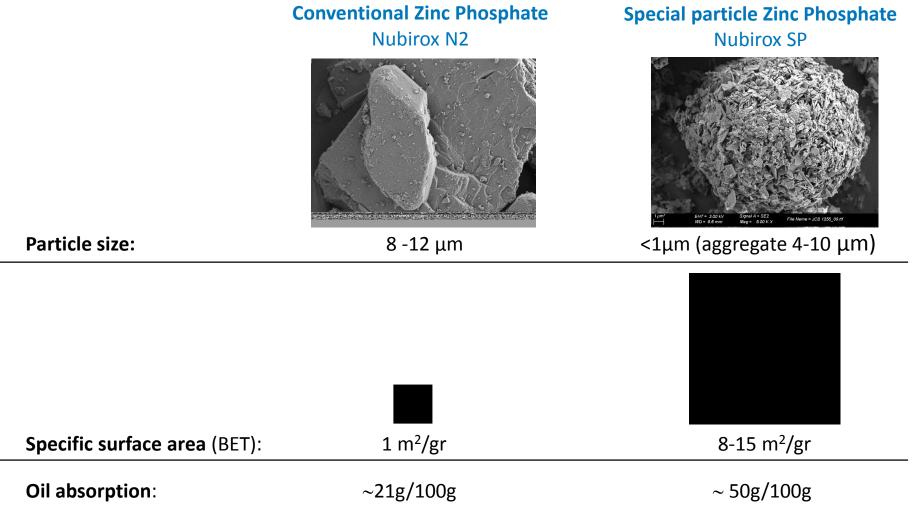
Lamellar primary crystals (<1µm)

Agglomerated spherical particles (>8 μm)



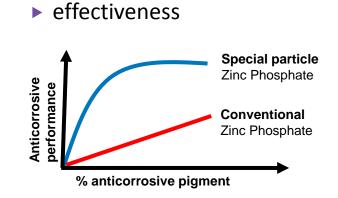


Zinc phosphate: same chemistry but different physics

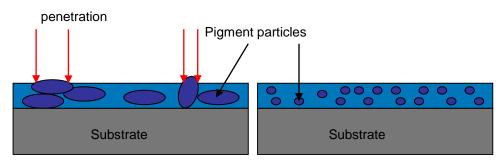




Zinc phosphate: same chemistry but different physics and performance



performance in thin coatings





• **Zinc phosphate:** performance in thin coatings

Conventional Zinc Phosphate Nubirox N2 Special particle Zinc Phosphate Nubirox SP





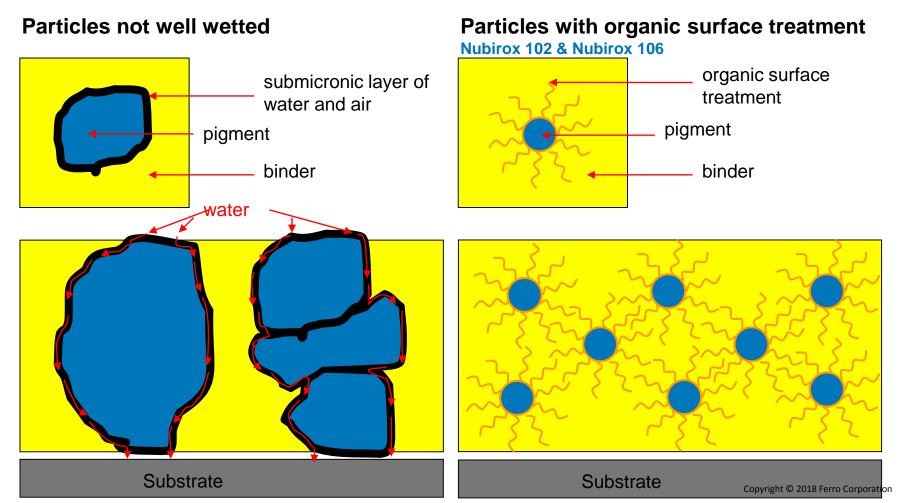
Solvent based system Long oil air drying alkyd resin CPV=35 10% anticorrosive pigment Application on satndardized cold rolled steel panels S-46 (Q-Panel) Dry film thickness~20µ **300 hours** of exposure in Salt Spray (ASTM B-

117).



Zinc based Nubirox

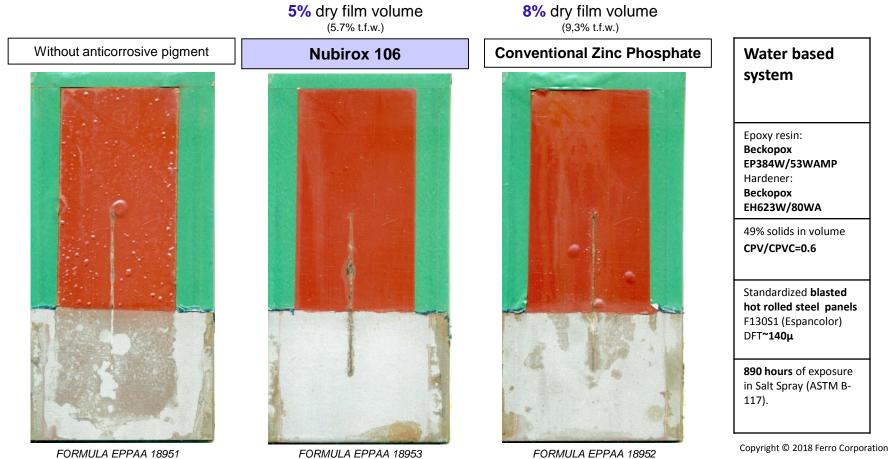
- Nubirox 100 series: Nubirox 102 & Nubirox 106
 - Modification with molybdate and organic surface treatement





Zinc based Nubirox

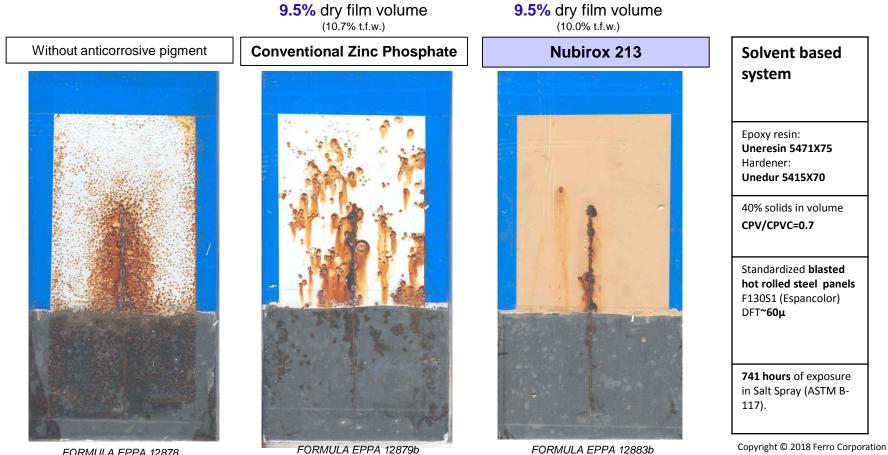
- Nubirox 106
 - Based on special particle Zinc Phosphate
 - High pigment effectiveness at low loading level in many SB and WB paint systems





Zinc based Nubirox

- Nubirox 213
 - Modification with Iron Phosphate
 - Specially suitable for alkyd and epoxy primers used to protect steel substrates



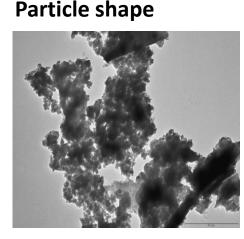
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FORMULA EPPA 12879b

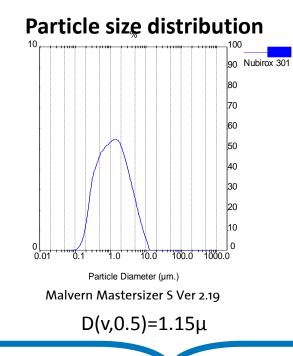


Non Zinc based Nubirox

- Nubirox 300 series
 - Nubirox 301 & Nubirox 302 based on Calcium Strontium Phosphosilicate



SEM (scanning electron microscope)



Specific surface area

	Specific surface area (m2/g)
Zinc Phosphate	1
Nubirox 301	21

Particle characterization:

Elemental particles $<1\mu$ forming aggregates and agglomerates up to $<10\mu$

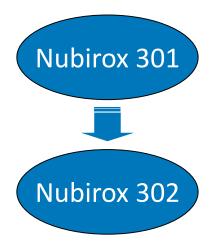
- More active surface (allows lower pigment dosage)
- Lower effect on gloss (DTM applications)



Non Zinc based Nubirox

Nubirox 302

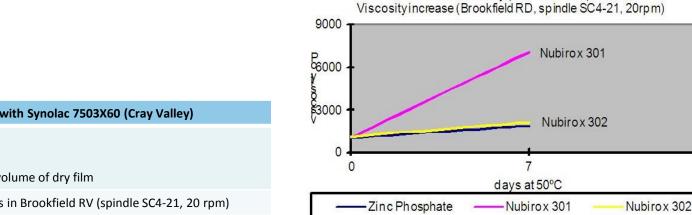
Organic surface treatment to improve binder compatibility and performance



Its alkalinity makes it reactive with acidic binders, like short oil alkyds, but not with main long oil alkyds (usually with low acid values).

Its organic treatment protects the pigment from reacting with the acid binder.

Paint Stability (ASTM D1849)



Short Oil Alkyd primer with Synolac 7503X60 (Cray Valley)

50% solids in volume

PVC/CPVC=0.7

6% Active pigment in volume of dry film

Viscosity measurements in Brookfield RV (spindle SC4-21, 20 rpm)

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Agenda

Anticorrosive pigments:

- What is corrosion? Mechanism of corrosion protection
- Nubirox anticorrosive pigments
 - Zinc based Nubirox: mechanism, particle shape and modifications
 - Non-Zinc based Nubirox: mechanism, particle and modifications

Anticorrosive coating formulation:

- Formulation parameters
- Examples of coating formulation:
 - Replacement of conventional Zinc phosphate in a SB Alkyd primer
 - Improving corrosion protection of WB DTM coatings

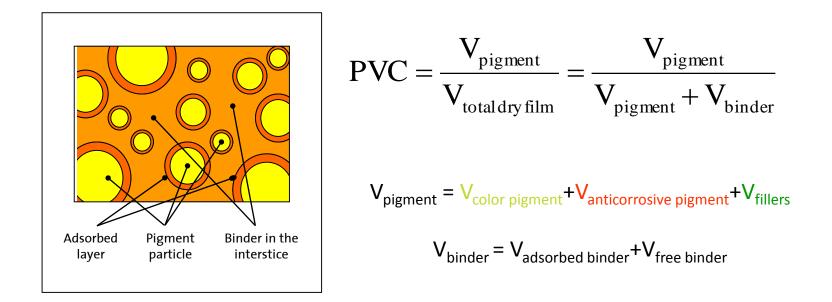






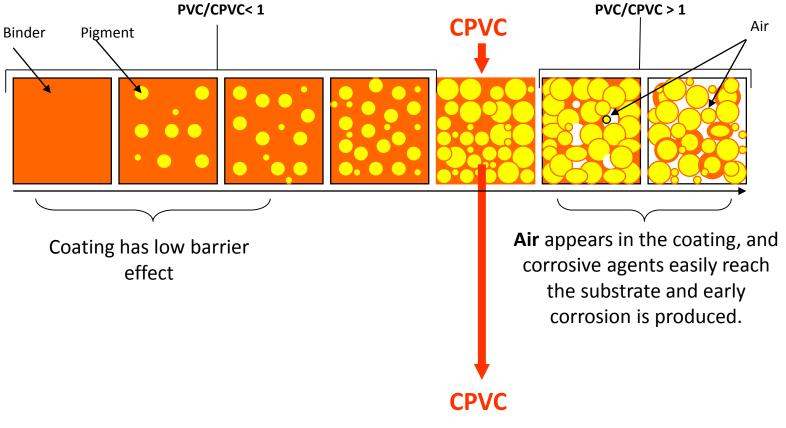
PVC "Pigment volume concentration"

> A paint film is a volume: formulation parameters must be fixed in volume units.





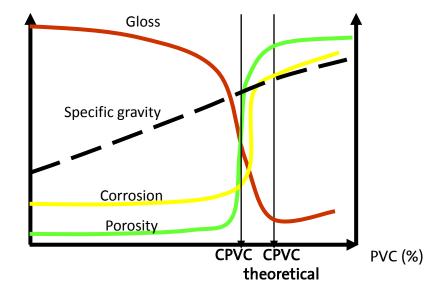
CPVC "Critical pigment volume concentration"



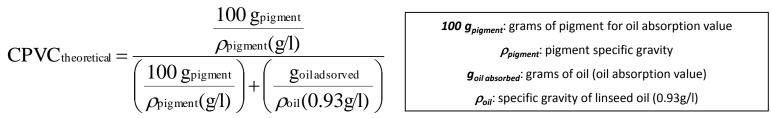
CPVC is just the **PVC** where there is just enough binder to wet all the pigments and fill the voids between particles.



PVC/CPVC ratio

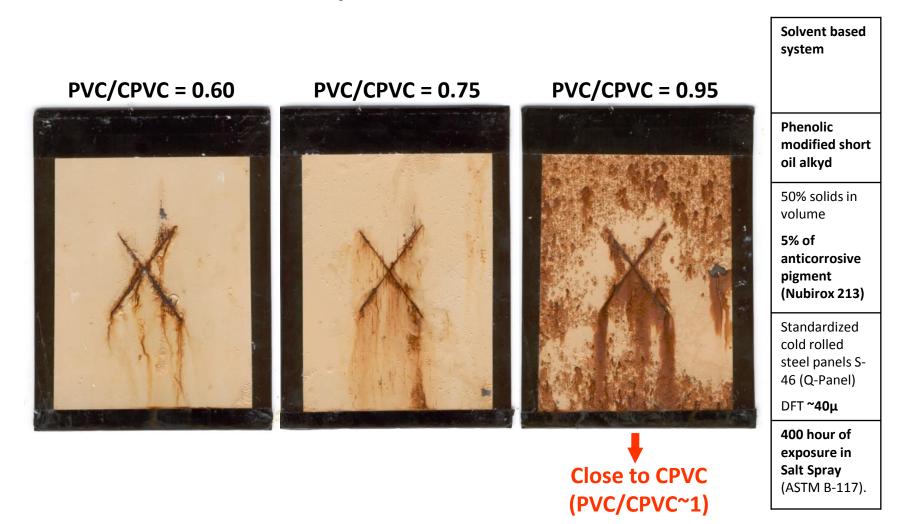


- **<u>CPVC</u>**: Characteristic of each pigment package and binder. Experimental.
- Theoretical CPVC: Calculated as the CPV for 100 grams of pigment and the grams of oil according to the oil absorption.





Effect of PVC/CPVC ratio on performance





SB Alkyd primer:

Replacement of conventional Zinc Phosphate

Direct replacement

Replacement 1:1 in weight

Reformulation

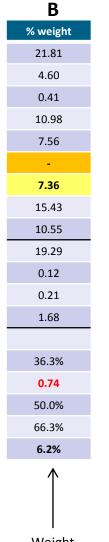
Differences only due to anticorrosive pigment effectiveness



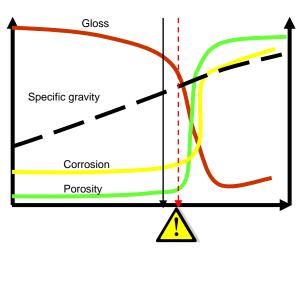


		Α
FORMULA	FUNCTION	% weight
Synolac 7503X60	Alkyd resin	21.81
Bentone 34 (10% in xylene)	Rheological additive	4.60
Calcium Naphtenate 4%	Wetting agent	0.41
Xylene	Solvent	10.98
Tioxide TR92	Titanium dioxide	7.56
Zinc Phosphate	Antic. Pigment	7.36
Nubirox 106	-	
Micral 2	Calcium carbonate	15.43
CBI-5 Talc	Micro talc	10.55
Synolac 7503X60 Alkyd resin		19.29
Cobalt Naphtenate 6%	Dryer	0.12
Synresol E-22	Anti-skinning agent	0.21
Dowanol PM	Solvent	1.68
Pigmen	t Volume Concentration	36.1%
	0.70	
Non-v	50.0%	
Non-	volatile contents, weight	66.3%
Anticorrosive pig	ment volume in dry film	6.0%

	Specific gravity (g/cm³)	Oil absorption (g oil/100g pig)
Zinc Phosphate	3.3	20
Nubirox 106	3.2	40



Λ



Weight replacement less free binder



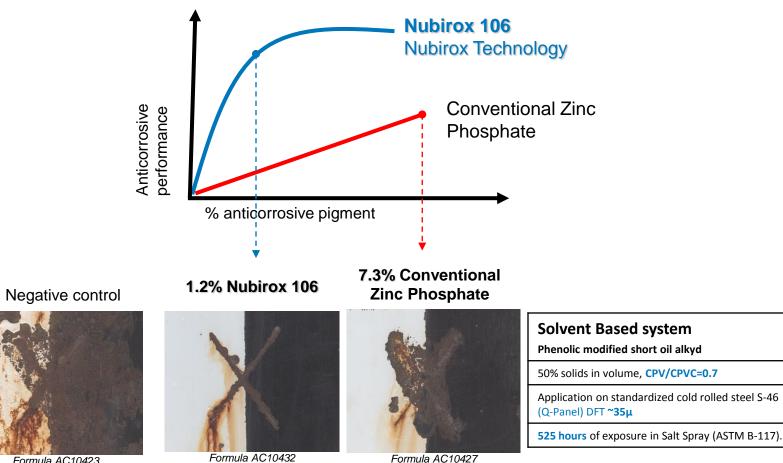
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Cobalt Naphtenate 6%	Dryer	0.12
Synresol E-22	Anti-skinning agent	0.21
Dowanol PM	Solvent	1.68
Pigmer	t Volume Concentration	36.1%
	0.70	
Non-v	olatile contents, volume	50.0%
Non-	volatile contents, weight	66.3%
Anticorrosive pig	ment volume in dry film	6.0%

	Specific gravity	Oil absorption
	(g/cm³)	(g oil/100g pig)
Zinc Phosphate	3.3	20
Nubirox 106	3.2	40

В		С	D
% weight		% weight	% weight
21.81	个	23.86	22.66
4.60		4.70	4.68
0.41		0.39	0.40
10.98		10.60	10.99
7.56		7.51	7.49
-		-	-
7.36		7.48	1.24
15.43	\checkmark	14.12	18.36
10.55	\mathbf{V}	9.66	12.56
19.29	小	19.70	19.60
0.12		0.13	0.13
0.21		0.20	0.12
1.68		1.68	1.69
36.3%		33.6%	35.4%
0.74		0.70	0.70
50.0%		50.0%	50.0%
66.3%		65.6%	65.7%
6.2%		6.0%	1%
\uparrow		\uparrow	\uparrow
Weight replacement			Cost-effective reformulation
less free binder			Copyright © 2018 Fer



Nubirox 106: Pigment effectiveness at low loading level



Formula AC10423

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WB Alkyd DTM for multisubstrate aplication:

Addition of anticorrosive pigments

Direct replacement

Replacement in weight of color pigment or extender

Reformulation

Differences only due to anticorrosive pigment effectiveness





		Α	В
FORMULA	FUNCTION	% weight	% weight
Water		8,99	8,99
Byk 024	Defoamer	0,12	0,12
Disperbyk 190	Dispersing agent	1,52	1,52
Tioxide TR92	Titanium dioxide	28,77	24,77
Nubirox 302	Antic. Pigment	-	4,00
Nubirox 106	Antic. Pigment	-	-
Uradil AZ760 Medium oil alkyd emulsion		58,12	58,12
Additol VXW4940 (1:1 water)	Drier	1,28	1,28
Nubirox FR-10	"Flash rust" inhibitor	0.50	0.50
Byk 348	Levelling agent	0.23	0.23
Acrysol RM-8W	PU-thickener	0,47	0,47
	Pigment Volume Concentration	19,3%	20,2%
	0.36	0.40	
	49,7%	50,1%	
	Non-volatile contents, weight	61,3%	61,4%
Anticorros	ive pigment volume in dry film	0%	3,7%

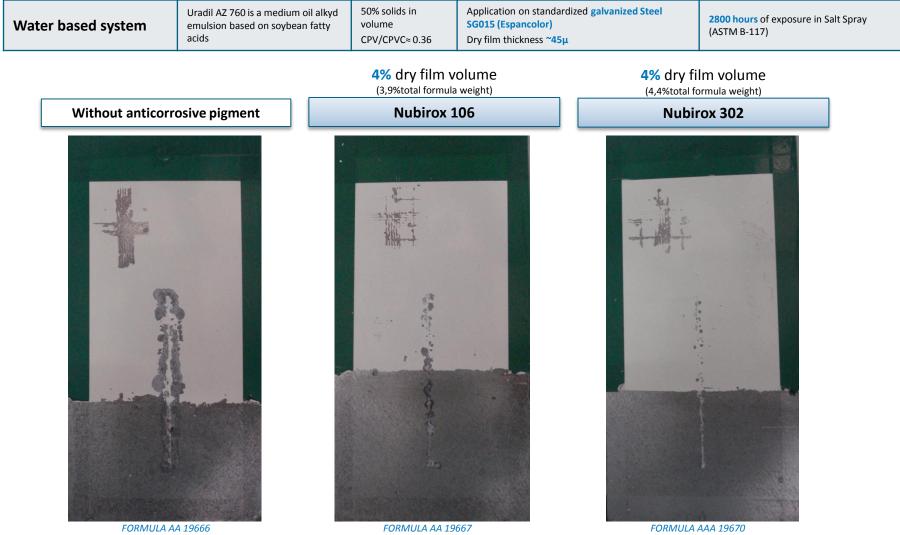
	58,12	
	1,28	
	0.50	Gloss
	0.23	
	0,47	
		Specific gravity
	20,2%	
	0.40	
	50,1%	Corrosion
	61,4%	
	3,7%	Porosity
	Î	
	TiO ₂ Weight	
	replacement	
1	ess free binder	

	Specific gravity	Oil absorption
	(g/cm³)	(g oil/100g pig)
Titanium dioxide	4,1	21
Nubirox 302	2,9	45



			Α	В		С		D	
FORMULA		FUNCTION	% weight	% weight		% weight		% weight	
Water			8,99	8,99		8,90		9,56	
Byk 024		Defoamer	0,12	0,12		0,13		0,12	
Disperbyk 190		Dispersing agent	1,52	1,52		1,38		1,43	
Tioxide TR92		Titanium dioxide	28,77	24,77	\checkmark	21,77	\checkmark	23,07	
Nubirox 302		Antic. Pigment	-	4,00		4,38	· ·	-	
Nubirox 106		Antic. Pigment	-	-		-		3,87	
Uradil AZ760		Medium oil alkyd emulsion	58,12	58,12	\wedge	60,84	\wedge	60,04	
Additol VXW4940 (1:1 water)	Drier	1,28	1,28		1,34		0,66	
Nubirox FR-10		"Flash rust" inhibitor	0.50	0.50		0.53		0.52	
Byk 348		Levelling agent	0.23	0.23		0.24		0.24	
Acrysol RM-8W		PU-thickener	0,47	0,47		0,49		0,49	
					'				
	Pi	gment Volume Concentration	19,3%	20,2%		18,2%		18,8%	
		PVC/CPVC	0.36	0.40		0,36		0,36	
	Ν	Non-volatile contents, volume	49,7%	50,1%		49,7%		49,7%	
	I	Non-volatile contents, weight	61,3%	61,4%		60,1%		60,8%	
	Anticorrosive	e pigment volume in dry film	0%	3,7%		4,0%		4,0%	
				Î		\uparrow		\uparrow	
	Specific gravity	Oil absorption							
	(g/cm³)	(g oil/100g pig)		TiO ₂ Weight		eformulation a		eformulation	
Titanium dioxide	4,1	21		replacement less free binder	Sa	ame PVC/CPV	C s	ame PVC/CP	VC
Nubirox 302	2,9	45							





Gloss (60º): 93

Gloss (20º): 79

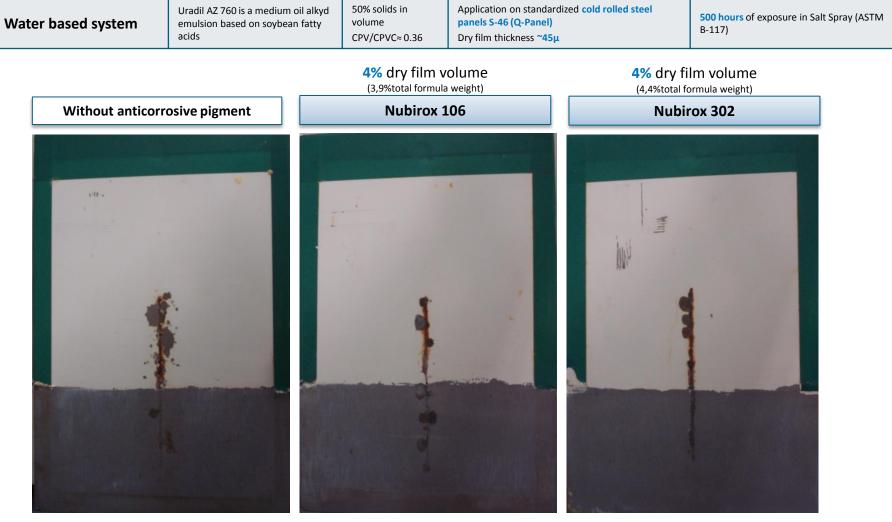
Gloss (60º): 98 Gloss (20º): 93

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Gloss (60º): 96

Gloss (20º): 85

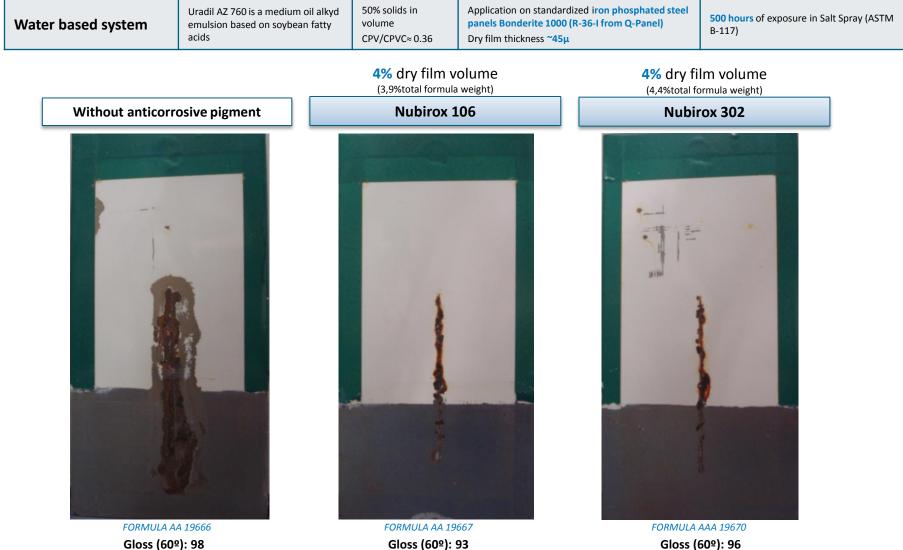




FORMULA AA 19666 Gloss (60º): 98 Gloss (20º): 93 FORMULA AA 19667 Gloss (60º): 93 Gloss (20º): 79 FORMULA AAA 19670 Gloss (60º): 96 Gloss (20º): 85

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Gloss (20º): 79

Gloss (60º): 98 Gloss (20º): 93

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Gloss (20º): 85



 Nubirox 302: good gloss/performance balance

Gloss

Panel evaluation	Control	4% Nubirox 106	4% Nubirox 302
Gloss 60º	98	93 <mark>(-5%)</mark>	96 (-2%)
Gloss 20º	93	79 <mark>(-15%)</mark>	85 (-9%)

Anticorrosive performance on Cold rolled steel

Panels exposed 500h in	Control	4%	4%
Salt Spray test		Nubirox 106	Nubirox 302
Rusting at the scribe	5	6	7
(ASTM D1654)	(3.5mm)	(3mm)	(2mm)
Rusting on the panel	8G	9G	9G
(ASTM D610)	(0.1%)	(0.03)	(0.03%)
Adhesion at the scribe	5	7	9
(ASTM D1654)	(15%)	(5%)	(1%)
Adhesion "cross cut" (ASTM B3359)	5B	5B	5B

Anticorrosive performance on Galvanized steel

Panels exposed 2800h in Salt Spray test	Control	4% Nubirox 106	4% Nubirox 302
Rusting at the scribe	5	7	9
(ASTM D1654)	(3.5mm)	(1.5mm)	(0.5mm)
Rusting on the panel	8G	7G	9
(ASTM D610)	(0.1%)	(0.3%)	(0.03%)
Adhesion at the scribe	2	6	9
(ASTM D1654)	(50%)	(10%)	(1%)
Adhesion "cross cut" (ASTM B3359)	ОВ	1B	1B

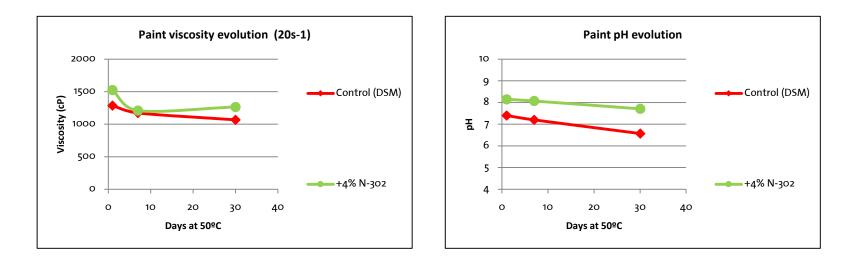
Anticorrosive performance on Phosphated steel

Panels exposed 500h in	Control	4%	4%
Salt Spray test		Nubirox 106	Nubirox 302
Rusting at the scribe	4	7	7
(ASTM D1654)	(6mm)	(1.5mm)	(1.5mm)
Rusting on the panel	7G	8G	9G
(ASTM D610)	(0.3%)	(0.1%)	(0.03%)
Adhesion at the scribe	0	8	9
(ASTM D1654)	(90%)	(2%)	(1%)
Adhesion "cross cut" (ASTM B3359)	4B	3В	18



Nubirox 302: good paint stability

Package stability (ASTM D1849): Viscosity, pH and settling evolution after 7 and 30 days at 50°C.



	Settling (ASTM D-869)		
	initial	7 days at 50°C	30 days at 50°C
Control	10	6	2
+4% N-302	10	8	6



Conclusions

Anticorrosive pigments:

- Not only is the chemistry important...
 also physical properties of pigment particles:
 - More active surface
 - Better performance in thin film systems
- Modifications improve performance of Zinc based pigments
- Non Zinc based anticorrosive pigments benefits

Anticorrosive coating formulation:

- Bear in mind formulation parameters
 - Adjust free binder volume to the desired properties
 - Pigment replacement in weight could be dangerous
 - Benefits of cost efficient replacements









Thank you

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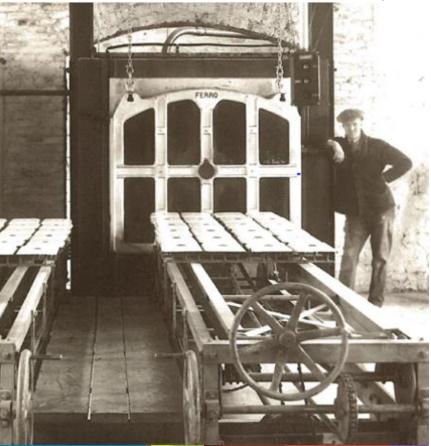
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- Founded 1919 as Ferro Enameling Company in Cleveland, Ohio USA
- Worldwide leader in production of glass enamels, porcelain enamels, ceramic tile coatings and high performance pigments
- Approximately 5,680 associates working in 27 countries
- 2016 sales of \$1.15 billion





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- Surface application technology
- Formulation









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