

A NOVEL WATERBORNE EPOXY RESIN FOR ZERO-VOC, TWO COMPONENT COATINGS

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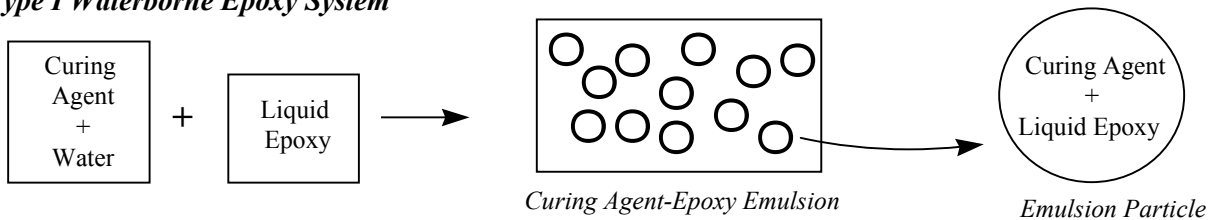
ABSTRACT

Novel waterborne epoxy resin technology has been developed for use in two-component ambient cure epoxy coatings. Unlike conventional solid epoxy dispersions which depend on co-solvents for coalescence, this technology offers the unique combination of good coalescence and zero VOC. Coatings formulated with this new resin exhibit properties on metal and concrete substrates that are equal or superior to existing waterborne epoxy coatings. Advantages include fast lacquer dry, fast development of rain resistance, little or no induction time, long pot life, universal colorant acceptance, and very low odor. Performance properties including handling properties, corrosion resistance, and flexibility will be reviewed, as well as Electrochemical Impedance Spectroscopy evaluation of barrier properties.

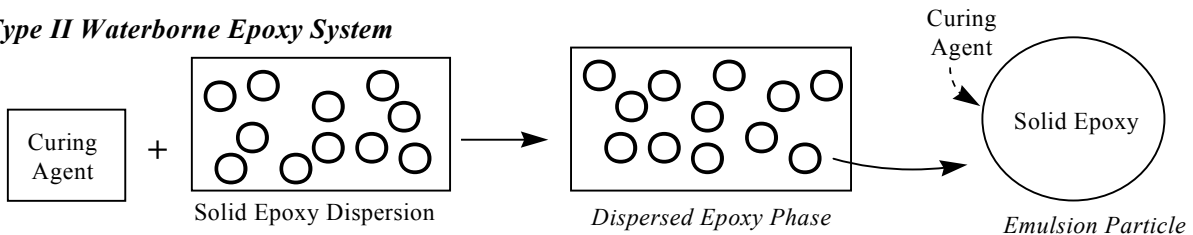
Introduction

Waterborne epoxy coatings have evolved into two fundamentally different technologies commonly identified as Type I and Type II systems. Type I systems are based on liquid epoxy resin. Typically, the amine curing agent serves as the emulsifier for the epoxy and the emulsion is formed when the A and B components of the paint are mixed together. The more recent Type II technology utilizes solid epoxy resin pre-dispersed in water and co-solvent. In Type I systems the dispersed resin particles contain both epoxy and curing agent. In Type II systems the dispersed resin particles contain only solid epoxy resin so that the curing agent must migrate from the aqueous phase into the dispersed epoxy particles for reaction to occur.

Type I Waterborne Epoxy System



Type II Waterborne Epoxy System



Type I systems can often be formulated to zero VOC, primarily because liquid epoxy exhibits good handling, flow, and coalescence without the aid of co-solvents. However, liquid epoxy systems cannot reach high viscosity through water evaporation alone but must depend on chemical reaction to increase viscosity. As a result, liquid epoxy systems are very slow to dry, often taking more than 6 hours to reach tack free.

As previously mentioned, Type I systems utilize amine curing agents to emulsify the liquid epoxy forming dispersed resin particles which contain both epoxy and amine. In addition, liquid epoxy (epoxide equivalent weight 190) is very rich in epoxide groups. The combination of concentrated epoxides and amine hydrogens in the same dispersed particle leads to very short pot lives.

Liquid epoxy with its short rigid backbone yields cured coatings with high hardness but low flexibility and low impact resistance. While suitable for cementitious applications, liquid epoxy coatings are often too brittle for use on metal substrates.

To overcome the limitations of liquid epoxy, waterborne systems based on high molecular weight solid epoxies were developed. Solid epoxies are supplied pre-dispersed at 50-55% solids in water and co-solvent. To aid in processing and to overcome the poor flow and coalescence of solid epoxies, 5-10% glycol ether is added to the dispersions thereby eliminating any possibility for zero VOC formulations.

Type II systems offer the handling and performance benefits associated with solid epoxy resins. Dry times are very fast due to lacquer dry of the high viscosity epoxy. Flexibility is improved due to the more flexible backbone of solid epoxy. Pot life is much longer due to the lower concentration of epoxides and amine hydrogens and also because amine must migrate from the aqueous phase into the dispersed epoxy particles before reaction can take place.

The principal weakness of Type II systems is their tendency to form heterogeneous films with epoxy rich and amine rich domains due to incomplete coalescence. Co-solvents and plasticizers are added at levels of one hundred to two hundred and fifty grams per liter to improve film formation and to extend pot life. During the pot life, as amine reacts with epoxy, the MFT of the polymer keeps increasing until the film can no longer coalesce. The end of pot life is not signaled by a viscosity increase but rather by a loss of gloss or a loss of barrier properties.

Novel Epoxy Resin Technology

A novel waterborne epoxy resin dispersion has been developed which incorporates the best characteristics of both Type I and Type II systems (see Table 1 below). The unique chemistry of this epoxy resin enables the formulation of a Type II system that retains the advantages of such systems including high epoxy equivalent weight (EEW), long pot life, and fast lacquer dry. However, coatings based on this new resin also exhibit desirable performance attributes previously only found with Type I waterborne epoxy systems including zero VOC and lower cost-in-use.

Table 1: Comparison of Type I and Type II Systems

	Type I Liquid Epoxy	Type II Solid Epoxy
Epoxy Equivalent Weight (EEW)	175-240	450-750 ★
VOC (lb/gal)	0-1★	2-3
Pot Life	1-3 hours	> 4 hours★
Drying Speed	Slow	Fast★
Drying Mechanism	Chemical Reaction	Lacquer Dry★
Epoxy Resin Cost	Lower Cost★	Higher Cost

★ New Epoxy Resin Technology exhibits these attributes.

This novel resin, commercially known as Ancarez™ AR550 resin, exhibits the following typical properties.

TABLE 2: Typical Resin Properties

Appearance, liquid	Milky white
Appearance, film	Clear, Glossy
Solids content (wt. %)	55
Solvent	water
Viscosity @ 77 °F (cP)*	100
Flash Point (°F) ²	> 480
Specific Gravity @ 77 °F	1.09
Weight per Gallon	9.1
Epoxy Equivalent Weight (EEW, g/eq) ³	1300 as supplied 715 based on solids
Volume Average Diameter (D _v , μ m)	0.5

* Brookfield viscosity, Spindle #3, 12 rpm

Important aspects of the Ancarez AR550 resin's properties include its volume average diameter (D_v) of 0.5 μm, consistent with other high-quality Type II dispersions. Particle size in Type II systems is important for two reasons. First, overall particle size distribution impacts film formation, emulsion stability and emulsion viscosity. Additionally, because the curing agent must penetrate and react with the epoxy resin in Type II systems, the smaller the particle size the greater the overall surface area of all the particles, and hence, the greater the opportunity for reaction between the curing agent and the epoxy resin.

Another important property of the Ancarez AR550 resin is its molecular weight distribution. Molecular weight distribution impacts film formation, intraparticle viscosity and cure kinetics in waterborne epoxy systems. Ancarez AR550 resin contains a significantly larger percentage of lower molecular weight material than other established Type II solid dispersion resins. The larger percentage of low molecular weight material in Ancarez AR550 resin allows it to coalesce

without the aid of co-solvents. Thus Ancarez AR550 resin can be readily formulated to zero VOC while retaining the film formation characteristics of Type II systems.

Formulations Based On The New Epoxy Resin Technology

Three typical coatings were formulated to evaluate the performance of the Ancarez AR550 resin in two component ambient cure epoxy systems. The three coatings evaluated were a low-VOC, 4:1 anticorrosive metal primer; an ultra-low VOC, 2:1 high gloss metal enamel; and, an ultra-low VOC, 2:1 concrete enamel (see Appendix for formulation specifics). Formulation attributes for these three coatings are presented in Table 3.

Table 3: Formulation Attributes

	Anti-Corrosive Metal Primer	High-Gloss Metal Enamel	Concrete Enamel
VOC (lb/gal)*	0.36	trace	trace
VOC (g/l)*	43	2-3	2-3
Mix Viscosity (cP)	500	1000	1100
Weight Solids (%)	63.0	59.4	60.6
Volume Solids (%)	47.5	47.3	48.8
PVC (%)	34.4	15.6	15.1
Resin Stoichiometry (Epoxy:Amine)	1.4:1	1.15:1	0.93:1

Formulating Guidelines

Three very important considerations when formulating waterborne epoxies are coalescence, stoichiometry, and stability. As previously mentioned, good coalescence is critical for uniform film formation and for good barrier properties. Ancarez AR550 resin exhibits very good coalescence when used with either Anquamine® 401 or 419 curing agents. To further improve properties such as gloss or pot life, aromatic epoxy diluents such as Epodil® 742 diluent (cresyl glycidyl ether) can be added to the Ancarez AR550 resin at approximately 5% (w/w) .

When formulating for corrosion resistance, 10-40% excess epoxy is desirable. When formulating for faster property development, 10-20% excess curing agent is desirable. A good balance of properties is obtained at 1:1 stoichiometry.

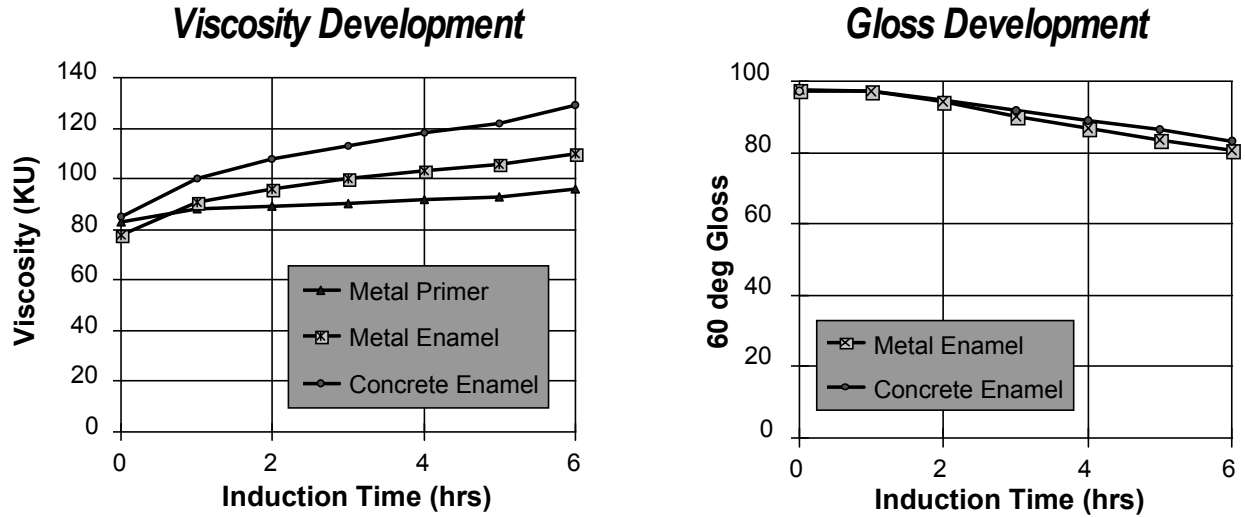
Pigments and high levels of dilution can de-stabilize either the epoxy side of the formulation or the curing agent side of the formulation. When pigmenting the epoxy dispersion, a pigment dispersing agent such as Disperbyk 190 dispersant should be added to avoid agglomeration of the epoxy dispersion. When pigmenting the curing agent side of the formulation, small amounts of acetic acid (0.2-0.5% based on curing agent weight) may be needed to improve water solubility and avoid separation. This is especially true when formulating with Anquamine 419 or similar curing agents.

Handling and Performance Results

Pot Life Characteristics

All three formulations (anticorrosive metal primer, high gloss metal enamel, and concrete enamel) based on the novel Ancarez AR550 resin exhibited the desirable long pot lives of Type II systems (4 - 6 hours).

Figures 1 and 2:



Analysis of the viscosity development and gloss development over the induction time revealed a gradual increase in viscosity with a corresponding loss in gloss. End of pot life was shown to occur with the coating's loss of gloss, revealing its decreasing ability to coalesce.

Table 4: Summary of Pot Life and Dry Time Evaluation

Formulation	Pot Life	Set-to-Touch	Light Traffic	Heavy Traffic
Metal Primer	6 hr	20-30 min	-	-
Metal Enamel	4 hr	20-30 min	-	-
Concrete Enamel	4 hr	20-30 min	24 hr	72 hr

Sample Preparation

For this evaluation, the A and B components were mixed, let down with water, and spray applied to shot blasted steel (2 mil profile). The coatings (3-4 mil DFT) were allowed to cure for 14 days prior to testing. Bonderite 1000 panels were used for humidity and electrochemical impedance spectroscopy evaluation.

Early Rain Evaluation

The anticorrosive metal primer, high-gloss metal enamel, and concrete enamel based on the Ancarez AR550 resin were evaluated for early rain resistance by periodically applying DI water to sections of a freshly applied coating. Coatings were judged to be rain resistant when they exhibited complete resistance to blistering and softening and only slight downglossing was observed.

This evaluation revealed that after a cure of only 2-3 hours (see Table 5 below) the coatings were resistant to rain. Type II waterborne epoxy systems with solvent require over 6 hours of cure time to achieve an equal degree of rain resistance.

Table 5: Summary of Early Rain Evaluation

Formulation	Early Rain Resistance
Anticorrosive Metal Primer	3 hours
High-Gloss Metal Enamel	3 hours
Concrete Enamel	3 hours

Other Performance Characteristics

Standard performance evaluations including pencil hardness, Persoz hardness, dry and wet adhesion, humidity resistance, salt fog, flexibility, and direct and reverse impact resistance were also conducted on the anticorrosive metal primer, high-gloss metal enamel and concrete enamel formulations.

Results from these test (summarized in Table 7, 8 and 9) show that all three formulations based on Ancarez AR550 resin deliver equal or superior performance characteristics as compared to conventional solid resin dispersions, however at ultra-low VOC and a lower cost-in-use.

Table 7: Hardness and Adhesion Evaluation

Formulation	Pencil Hardness 14 day cure scratch	Persoz Hardness ASTM D4366	Dry Adhesion ASTM D3359	Wet Adhesion ASTM D3359**
Metal Primer	H	140	5B	5B
Metal Enamel	F	190	5B	4B
Concrete Enamel	F	218	5B	4B

** 14 day cure; 1 week Cleveland Humidity exposure

Table 8: Humidity and Corrosion Resistance Evaluation

Formulation	Humidity Resistance ASTM D-4585	Salt Spray CRS B1000 2-3 mils DFT
Metal Primer	Pass 500 hr	Pass 1000 hr
Metal Enamel	Pass 500 hr	Pass 1000 hr
Concrete Enamel	Pass 500 hr	—

Table 9: Flexibility and Impact Resistance Evaluation

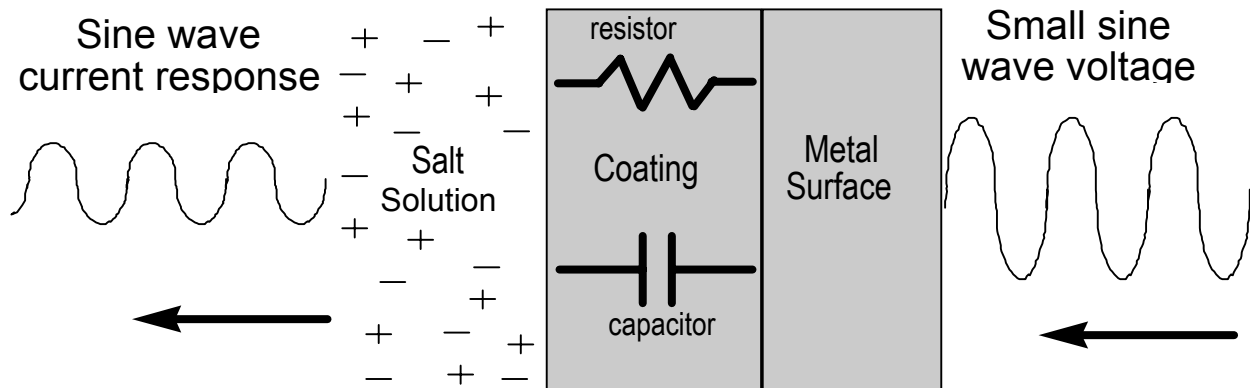
Formulation	Mandrel Bend	Direct Impact	Reverse Impact
Metal Primer	pass ½ “	16 in-lb	4 in-lb
Metal Enamel	pass ¼”	50 in-lb	4 in-lb
Concrete Enamel	-	60 in-lb	10 in-lb

Performance Evaluation Using Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a relatively new technique for measuring the barrier properties of coatings. EIS experiments are typically 24 hours in duration and correlate well with long term tests such as salt fog and prohesion.

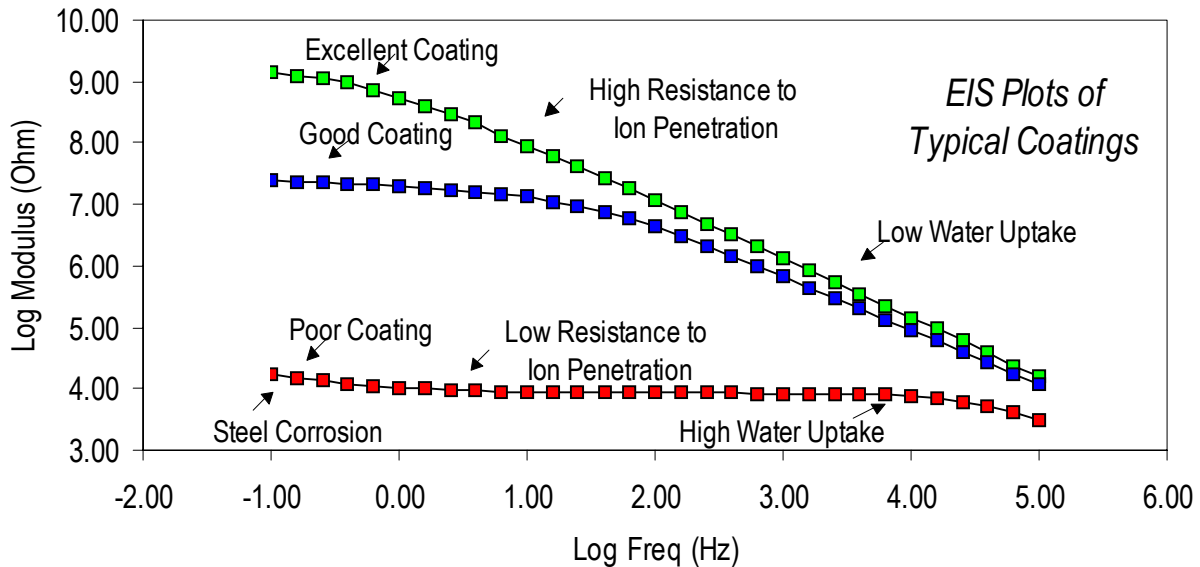
As shown in Figure 3, EIS involves exposing a coated steel panel to a salt water solution. A small AC voltage is applied to the steel panel. The electrical current that passes through the coating into the salt water is measured. By varying the frequency of the AC voltage, it is possible to separate and measure the water uptake of the coating (capacitance) and the resistance of the coating to sodium and chloride ion penetration (pore resistance).

Figure 3: EIS Diagram (note change of resistor and capacitor labels)



Resistance (Log Modulus (ohm)) is graphed vs. frequency to obtain a plot which measures both water uptake at high frequency and ion resistance at low frequency. A good barrier coating will exhibit low water uptake and high resistance to ion penetration as illustrated in Figure 4.

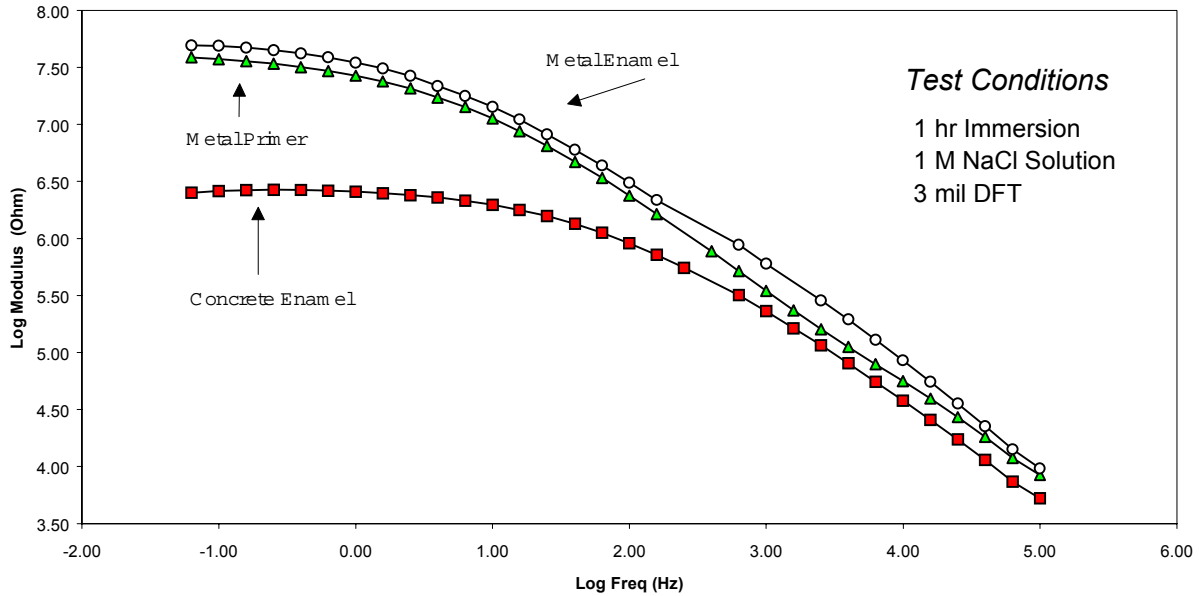
Figure 4: Sample EIS Plots of Excellent, Good, and Poor Barrier Coating



Experimental Results

The anticorrosive metal primer, high-gloss metal enamel, and concrete enamel were each spray applied (3-4 mil DFT) to shot blasted steel panels (2 mil profile). Using a Gamry FAS1 Potentiostat with EIS 900 software, measurements were taken after 1 hours of immersion in 1 M NaCl solution for all three formulations.

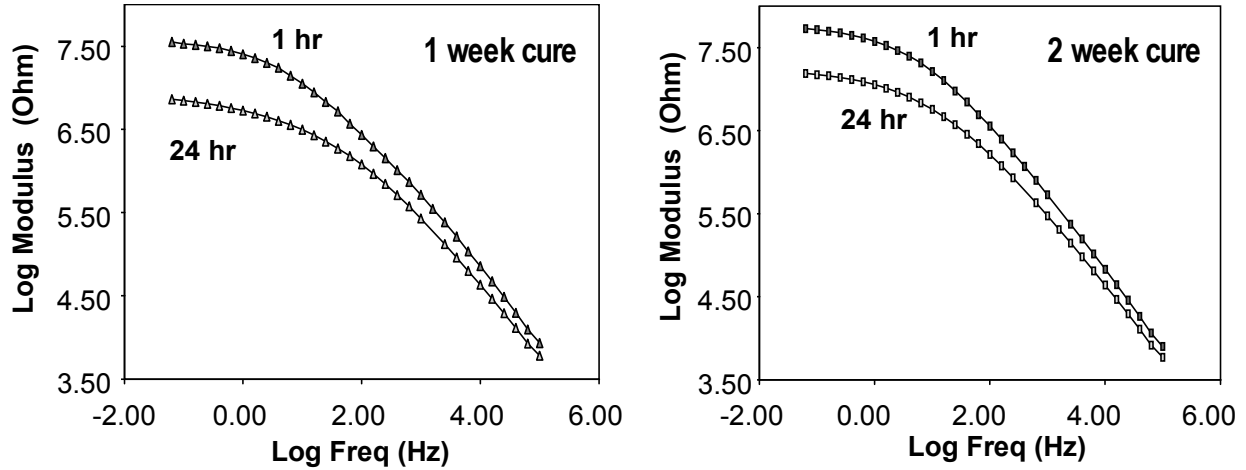
Figure 5: EIS Results



EIS results (see Figure 5) indicate that all three formulations showed very good resistance and capacitance (greater than 10^6 ohms) after 1 hour immersion. This data indicates that the coatings are highly resistant to ion penetration, particularly in the case of the anticorrosive metal primer and high-gloss metal enamel where such properties are extremely desirable.

A comparison of the extent of cure was also undertaken using EIS to evaluate the metal primer's corrosion resistance. For this evaluation, the metal primer formulation based on Ancarez AR550 resin was applied to 3-4 mil DFT over shot blasted steel (2 mil profile). Separate panels were cured over 7 and 14 days, and then evaluated, again using the Gamry FAS1 Potentiostat with EIS 900 software. Measurements were taken after 1 hour and 24 hours immersion in 1 M NaCl solution.

Figure 6 and 7: Metal Primer Corrosion Resistance After 1 and 2 Week Cure



EIS results indicate that after a 1 week cure, the metal primer coating is very highly resistant to salt water (as measured by the y-axis). Panels cured for 2 weeks show an even greater resistance to ion penetration, demonstrating the anticorrosive properties of the Ancarez AR550 resin-based metal primer formulation.

Summary

A novel waterborne solid epoxy resin designed for two component, ambient cure epoxy systems displays the desirable characteristics of both Type I and Type II systems. Typical industrial maintenance coatings formulated with the Ancarez AR550 resin were shown to deliver equal or superior performance characteristics, particularly early rain resistance, as compared to conventional solid resin dispersions, however at ultra low VOC and lower cost. Based on the performance evaluations that were conducted, recommend applications include OEM, industrial maintenance and transportation coatings; floor sealers and paints; anticorrosive primers, mid-coats and top coats; and industrial coatings.

APPENDIX

Ancarez™ AR550 Epoxy Resin / Anquamine® 419 Curing Agent

Starting Point Formulation 4 : 1 Anticorrosive Metal Primer

	Pounds	Gallons
<i>Part A</i>		
---Charge into mixing vessel:		
Ancarez AR550 Epoxy Resin	114.92	12.63
---Add at slow speed:		
De-ionized Water	81.59	9.78
Disperbyk 190 Dispersant	16.09	1.83
Dee Fo PI-4 Defoamer	3.45	0.41
Byk-022 Defoamer	0.57	0.07
---Mix for 10 min. at slow speed, then add:		
Red Iron Oxide	77.69	1.81
Zeeospheres 400	77.69	4.07
Sparwite Barytes	77.69	2.12
Wollastocoat 10ES	77.69	3.24
Strontium Phosphosilicate	114.92	4.77
Mica 325	7.77	0.33
---High speed disperse to Hegman 6+, then let down with:		
Ancarez AR550 Epoxy Resin	344.76	37.89
Acrysol RM-8W Rheology Modifier	<u>9.19</u>	<u>1.06</u>
	1004.0	80.0
 <i>Part B</i>		
---Charge into mixing vessel:		
Anquamine 419 Curing Agent	71.71	7.93
De-ionized water	<u>100.69</u>	<u>12.07</u>
	172.4	20.0

Ancarez AR550 Epoxy Resin / Anquamine 401 Curing Agent

Starting Point Formulation Ultra Low VOC 2 : 1 High Gloss Metal Enamel

	Pounds	Gallons
<i>Part A</i>		
---Charge into mixing vessel:		
Ancarez AR550 Epoxy Resin	594.9	65.37
---Add at slow speed a premix of:		
Acrysol RM-8W Rheology Modifier	2.1	0.25
De-ionized Water	<u>8.8</u>	<u>1.06</u>
---Mix for 30 min. at slow speed	605.8	66.7
 <i>Part B</i>		
---Add in order to the grind vessel:		
De-ionized water	65.3	7.83
Dee Fo PI-4 Defoamer	3.3	0.39
BYK-022 Defoamer	0.7	0.08
Anquamine 401 Curing Agent	32.7	3.59
---Mix for 10 min. or until curing agent is incorporated		
---Then add:		
Glacial Acetic Acid	0.5	0.06
---Mix for 5 min.		
---Then add:		
TR-92 Titanium Dioxide	250.0	7.35
---Grind to Hegman 7+		
---Then add:		
De-ionized water	58.1	6.97
Anquamine 401 Curing Agent	47.4	5.21
BYK-341 Flow Additive	2.0	0.25
---Mix for 15 min. at slow speed		
---Then add at slow speed:		
Acrysol RM-8W	12.0	1.38
RM-2020 Thickener	<u>2.0</u>	<u>0.22</u>
---Mix for 30 min. at medium speed	474.0	33.3

Ancarez AR550 Epoxy Resin / Anquamine 401 Curing Agent

Starting Point Formulation Ultra Low VOC 2 : 1 Concrete Enamel

	Pounds	Gallons
<i>Part A</i>		
---Charge into mixing vessel:		
Ancarez AR550 Epoxy Resin	594.9	65.37
---Add at slow speed a premix of:		
Acrysol RM-8W Rheology Modifier	2.1	0.25
De-ionized Water	<u>8.8</u>	<u>1.06</u>
---Mix for 30 min. at slow speed		
	605.8	66.7
 <i>Part B</i>		
---Add in order to the grind vessel:		
De-ionized water	72.3	8.67
Dee Fo PI-4 Defoamer	2.5	0.30
BYK-022 Defoamer	0.9	0.10
Anquamine 401 Curing Agent	28.5	3.13
---Mix for 10 min. or until curing agent is incorporated		
---Then add:		
Glacial Acetic Acid	0.7	0.08
---Mix for 5 min.		
---Then add:		
TR-92 Titanium Dioxide	250.0	7.35
---Grind to Hegman 7+		
---Then add:		
De-ionized water	27.7	3.32
Dee Fo PI-4 Defoamer	0.8	0.10
BYK-022 Defoamer	0.4	0.05
Anquamine 401 Curing Agent	70.0	7.69
BYK-341 Flow Additive	2.0	0.25
---Mix for 15 min. at slow speed		
---Then add at slow speed:		
Acrysol RM-8W	17.0	1.96
RM-2020 Thickener	<u>3.0</u>	<u>0.33</u>
---Mix for 30 min. at medium speed		
	475.8	33.3