
2K Waterborne Epoxy Systems: Technology Overview and New Developments

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ABSTRACT

Waterborne epoxy coatings were commercially introduced about 40 years ago, mainly as an environmentally friendly replacement to solvent-borne epoxies in countries with strong environmental and worker safety regulations. Their growth was mainly driven by the desire to reduce the emission of organic solvents. This technology grew most rapidly in the concrete protection market, though there is also use over metal substrates and for some OEM applications.

This paper will review the classification of waterborne epoxy coatings according to the type of epoxy resin being used. Type I systems are based on low molecular weight, liquid epoxy resin, and the curing agent typically doubles as the emulsifier for the resin. Type II systems are based on high molecular weight, solid epoxy resin dispersions. Properties like pot-life behavior, dry time and drying mechanisms (film formation) will be reviewed for both systems.

New developments in waterborne epoxy curing agent technology will then be described. At this time, their adoption is not driven principally by environmental regulations. Rather, they provide unique technical solutions to overcome well known problems that have remained unsolved for many years in our industry, like adhesion to green concrete, blistering promoted by osmotic pressure, poor stain resistance against acidic foods, and color stability.

INTRODUCTION

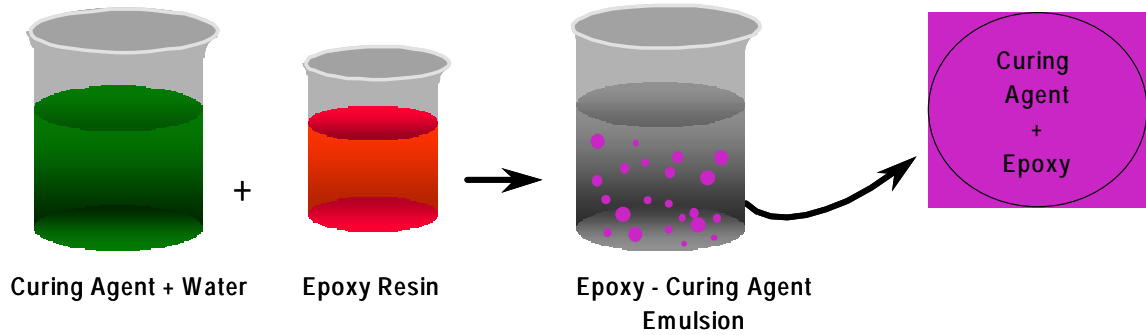
Epoxy coatings are extensively utilized in protective coatings and flooring markets due to their generally high level of mechanical properties, corrosion protection and chemical resistance. In the last few decades epoxy coatings have evolved from high VOC systems to more environmentally friendly technologies, like high solids coatings, solvent-free coatings, powder coatings, and waterborne coatings. This paper will focus on waterborne epoxy coatings.

In the area of waterborne epoxy coatings the technology has evolved along two fundamentally different routes commonly identified as Type I and Type II systems¹. Type I systems are based on liquid bisphenol A/F epoxy resins, with an EEW <250. Type II systems are based on higher molecular weight, solid epoxy resin dispersions.

Type I Waterbased Epoxy System

Figure 1

Mixing process for a typical Type I WB Epoxy System

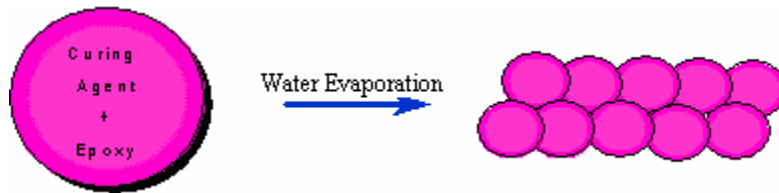


In Type I systems, the curing agent not only crosslinks the epoxy resins in the final film, but in the liquid state often also serves as the emulsifier for the epoxy resin. As a result, in these systems, immediately after mixing the emulsion particles contain both curing agent and epoxy resin, although there is usually also some amine in the aqueous phase. In contrast to the Type II systems described below, there is clearly less phase separation of the curing agent and resin. After application of the coating, water evaporates and the particles coalesce. Good coalescence is normally not an issue due to the low molecular weight of the ingredients and consequently high rates of diffusion, and coatings generally form that possess relatively uniform film morphology.

Figure 2

Type I WB epoxy film formation.

The curing agent and epoxy resin are both present in emulsion particles, and phase separation issues are minimal.



Type I systems can often be formulated to zero VOC coatings, primarily because liquid epoxy resins exhibit a good combination of handling, flow and film formation properties without the aid of co-solvents. Typical liquid epoxy resin (epoxide equivalent weight 190) consists of low molecular weight species, and therefore has a high concentration of epoxide groups. This high concentration and the close proximity of the active amine-hydrogen within the same dispersed particle leads to rapid reaction within the particle. As a result, the working life (pot life) of such systems are usually short, typically 2 hrs. Liquid epoxy with its short rigid backbone yields cured coatings with high hardness but low flexibility and low impact resistance. While suitable for cementitious substrates, liquid epoxy coatings can sometimes be too brittle for use on metal substrates, unless flexibility is introduced into the cured matrix from the amine curing agent.

Type II Waterbased Epoxy Systems

Figure 3
Mixing process for a typical Type II WB Epoxy System

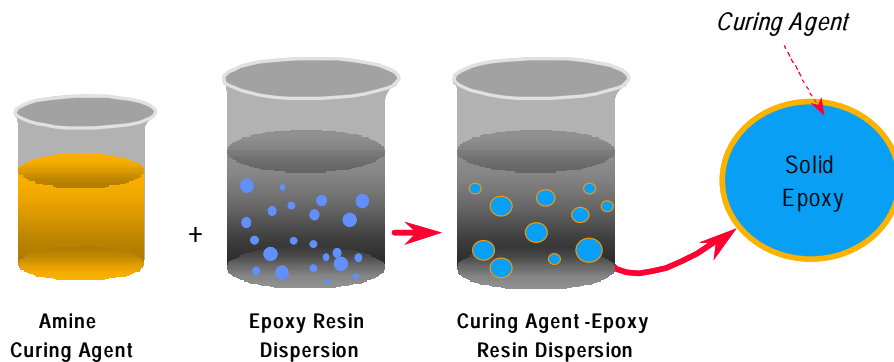
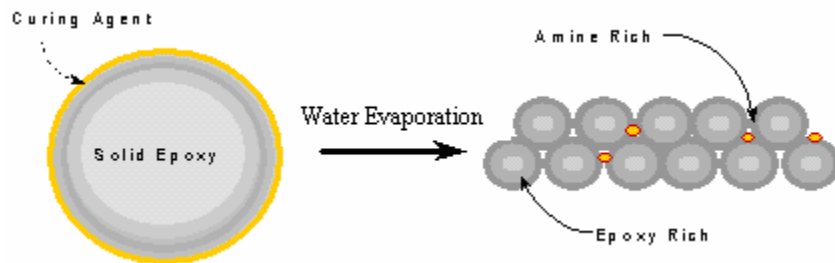


Figure 4
Type II WB epoxy film formation.
Curing agent reacts at surface and slows diffusion resulting in un-reacted epoxy at core



To overcome the limitations of the Type I approach, waterborne systems based on higher molecular weight solid epoxy resins were developed. Solid epoxies are supplied pre-dispersed at 50-55% solids in water and co-solvent, and always contain an emulsifier. 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.

With these systems the dispersed resin particles contain only solid epoxy resin. Therefore the curing agent must migrate from the aqueous phase into the dispersed epoxy particles for the crosslinking reaction to occur. As the coating coalesces, there is a greater tendency for films with a heterogeneous film morphology to develop. Stained cross sections of certain Type II coatings viewed through transmission electron microscopy have shown particle boundaries to be amine rich, further suggesting the presence of un-reacted epoxy resin in the particle cores.

Type II systems offer many of the handling and performance benefits associated with conventional solvent based solid epoxy resin formulations. Dry-to-touch times are very fast due to the lacquer dry of the high molecular weight resin, and impact resistance is improved due to the lower crosslink density relative to liquid epoxy formulations. Pot life is longer due to the lower concentration of epoxide groups and also because of the diffusion requirements for the amine curing agent, as previously discussed.

Type II epoxy systems generally result in films with inferior chemical resistance and poorer barrier properties than their solvent-borne counterparts. Co-solvents and plasticizers are added at levels of 100-150g/L to improve film formation and to extend pot life, so VOC's are higher than for Type I systems. During the pot life, as amine reacts with epoxy, the minimum film formation temperature (MFFT) of the polymer increases until the film can no longer coalesce. The end of pot life is often not signaled by a viscosity increase, but rather by a decrease in performance properties such as gloss or corrosion resistance, which only becomes evident after the film has been formed on a substrate. Typical properties of coatings based on these technologies are summarized in Table 1.

Table 1
Comparison of Type I and Type II Systems

Property	Type I Liquid Epoxy	Type II Solid Epoxy
Epoxy Equivalent Weight (EEW)	175-240	450-750
VOC (g/l)	0	100-300
Typical Pot Life	1-2 hours	> 4 hours
Typical Drying Speed	Slow	Fast
Key Drying Mechanism	Chemical Reaction	Lacquer Dry

Novel Curing Agent Technologies

New developments in waterborne epoxy curing agent technology will next be described. At this time, they are often not driven primarily by environmental regulations. Rather, they provide unique technical solutions to overcome well known problems that have remained unsolved for many years in our industry, like adhesion over green concrete, blistering promoted by osmotic pressure, poor stain resistance against acidic foods, and color stability

New Technology 1: Adhesion over Green Concrete

Conventional epoxy paints and flooring formulations are typically applied after the concrete is completely cured. The recommended wait is 28 days to insure that residual moisture is minimized and does not interfere with adhesion. Application prior to this period with 100% solids formulations has often resulted in complete failure at the epoxy/concrete interface.

A new waterborne curing agent was designed to allow an epoxy primer to apply over freshly poured concrete (green concrete). A study of primer and curing compound formulations based on this curing agent over green concrete fabricated with different finishes was performed by Construction Technology Laboratories (CTL), a highly respected independent laboratory based in Skokie, IL.

The primer was evaluated over two concrete formulations. A 27 MPa concrete mix was used to simulate a commercial floor. Concrete Formulation 1 was finished using a steel trowel while Concrete Formulation 2 was finished either by broom finish or a mild shot blast after three days.

Table 2
Concrete Formulations

Concrete Formulation 1	
Cement	213kg
Flash	45.8kg
Fine Aggregate	650kg
Coarse Aggregate	847kg
Water	115 liters
Admixture	0.5kg
W/C Ratio	0.45
Finish	Steel Trowel

Concrete Formulation 2	
Cement	213kg
Fine Aggregate	658kg
Coarse Aggregate	862kg
Water	128 liters
W/C Ratio	0.60
Finish	Broom or Shot Blast

The slabs were allowed to cure for 24 hours after which the forms were removed. Sides of the slabs were sealed to insure moisture did not escape laterally. Slabs that were finished by steel trowel and broom were coated at 24 hours. The third slab was allowed to set for three days prior to mild shot blasting then immediately coated with the primer formulation.

The primers were then checked for adhesion over green concrete, and as a curing compound membrane according to ASTM C309-C, which includes a water retention test, ASTM 156-98 that specifically describes how fresh concrete is coated and put into a special oven with low humidity, high temperature and high air flow for 3 days and then weighed to determine water retention.

Results over green concrete

Primer Adhesion: Adhesion strength and mode failure as measure by the dolly pull-off test is shown in Figures 5 and 6, for 7 and 30 day cures, respectively (see formulation in Table 3). As can be seen, the steel trowel finished concrete gave higher strength than broom and shot-blasted surfaces. In all cases, the bond strength over primed concrete was greater than over the unprimed concrete. In all cases adhesion was greater than 1.7 MPa, which is generally regarded as the standard industry requirement. The mode of failure was primarily within the concrete substrate for the steel troweled sample. In other cases, the mode of failure was located at a thin layer of concrete paste at the top surface of the concrete substrate.

Figure 5
Bond Strength after 7 and 30 days cure

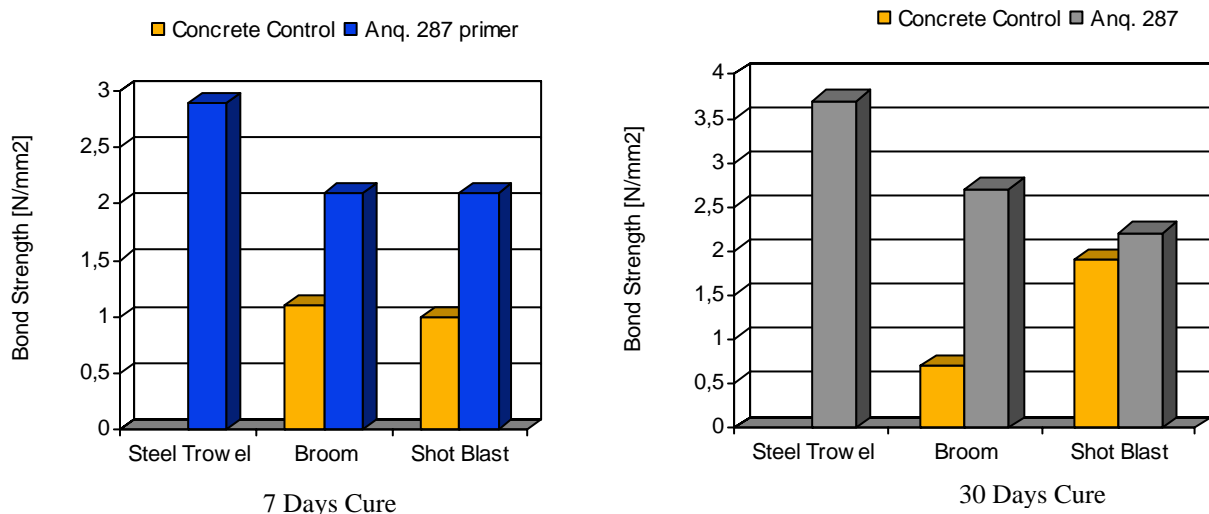
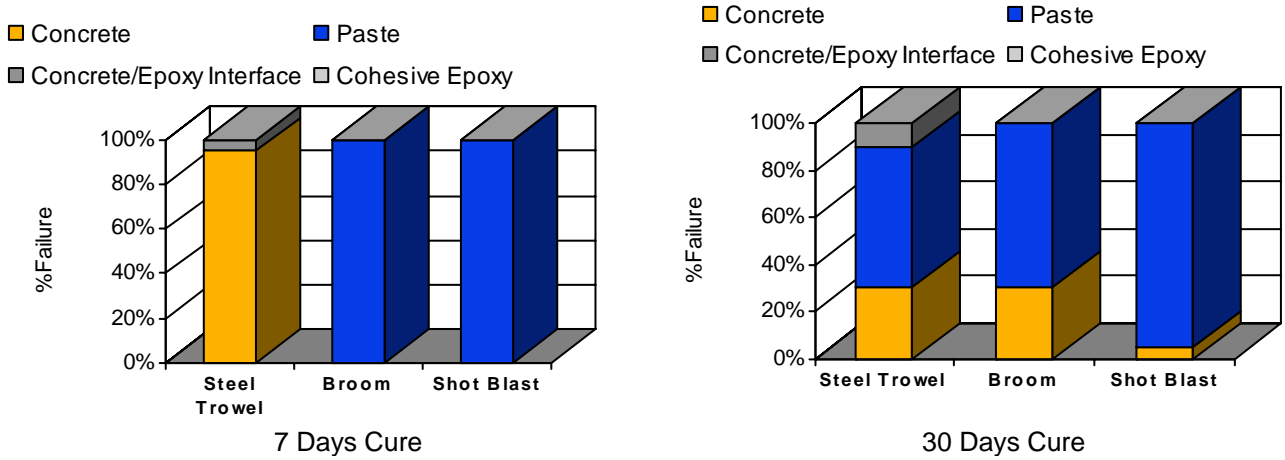


Figure 6
Mode of Failure after 7 and 30 days cure



Curing Compound: This test was run in triplicate and results were very reproducible, ranging from 0.51 to 0.53 Kg of water lost / m² during the test period. Based on these results, a primer formulated with the new curing agent will effectively work as a curing compound for freshly poured concrete. A key aspect to remember with this technology, however, is that the epoxy curing compound, unlike conventional acrylic or wax curing compounds, does not have to be removed. Instead, it can be used as a primer/curing compound in one and directly top-coated.

Table 3
Waterborne epoxy primer for Green Concrete and Curing Compound

Part A	
Raw Material	Parts by Weight
Liquid Epoxy Resin (EEW=190)	87
Epodil [®] 746	8
Component B	
Anquamine [®] 287	120
Dilution	
Water	173

New Technology 2: Moisture Vapor Transmission

A new Type I technology has been developed that results in faster drying times and which also allows for curing down to temperatures as low as 5°C. Formulations based upon it also have a more effective dilution profile, allowing the application of higher solids coatings at comparable viscosity. A significant characteristic of this curing agent to keep in mind is that it is an emulsion, compared to earlier curing agent technologies that are aqueous solutions.

Self-leveling floor formulations (see Table 4) have been developed which cure at > 3mm thickness to give a porous morphology, allowing the floor covering to be “breathable.” This breathability allows application to problem floors with high Moisture Vapor Transmission rates where conventional, 100% solids epoxy formulations delaminate. Permeability coefficients ranging from 30-140 times the values observed for floor formulations based on conventional systems have been observed. These unique properties address the limitations of conventional 100% solids epoxy formulations and earlier epoxy waterborne technologies.

Table 4
Breathable self-leveling waterborne epoxy formulation

Part A	
Raw Material	Parts by Weight
Anquamine® 701	11.0
Anquamine® 401	2.5
BYK® 045	0.7
TiO ₂ (R960)	3.8
Water	9.1
Cimbar 325	36.0
Cab-O-Sil 63	18.0
Quartz Sand (0.1 to 0.3 mm)	18.5
Xanthan Gum	0.4
Component B	
Liquid Epoxy Resin (EEW=190)	10.0

Blistering of synthetic-organic floor coverings, continues to be a major and costly concern that has been related to the flow of moisture vapor through the porous concrete in certain problematical installations. This flow can occur as a result of: 1) hydrostatic pressures or hydrostatic head; 2) capillary action; and 3) moisture vapor transmission. Hydrostatic pressures are found when a slab on grade is below the water table. Capillary action occurs where water is in contact with the underside of the slab. Moisture vapor transmission occurs where there is a higher relative humidity under the slab compared to the humidity above the slab. Although all contribute to the moisture flow through the slab, none by themselves or combined produces enough pressure to lift a well-adhered floor formulation. Epoxy flooring formulations provide an effective seal to block the moisture flow so blistering must involve another dynamic.

Osmotic pressure can produce forces that are several orders of magnitude higher than hydrostatic forces observed in uncoated concrete. Osmosis is defined as the spontaneous flow of a liquid through a semi-permeable membrane, from a dilute solution to a more concentrated solution. As a result, the liquid volume of the initially more concentrated solution increases until the hydrostatic pressure generated is in equilibrium with the osmotic pressure. The pressure generated by osmosis can greatly exceed other forces in concrete and ultimately yield in delamination of the floor coating. Three requirements must be fulfilled for osmosis to take place:

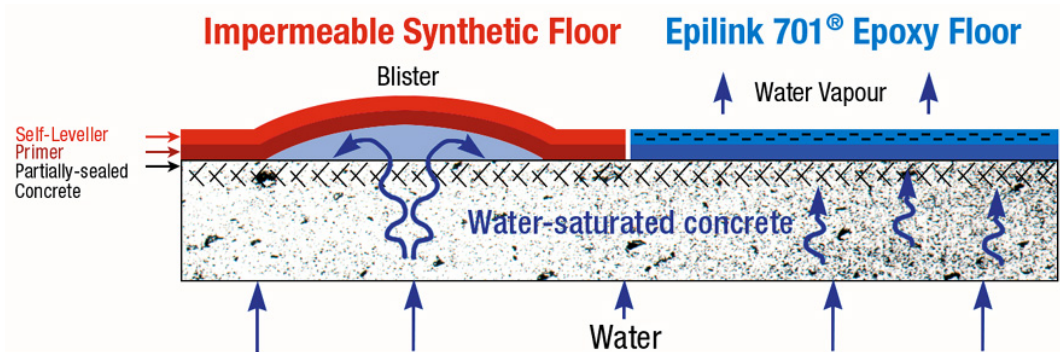
- (a) Presence of water (liquid and/or vapor)
- (b) Presence of salts or water-soluble organics
- (c) Presence of a semi-permeable membrane

All these conditions are typically found on concrete surfaces. Depending on the age of the concrete its moisture content can vary from about 4% when fully cured up to 18% in freshly prepared green concrete.

It is common practice to employ blast cleaning and high pressure water jetting to remove soluble salts that are readily available through several routes (salt water, ground water, de-icing or acid etching). However, their complete removal is virtually impossible. Concrete can act as a semi-permeable membrane itself, or a semi-permeable membrane is created when a coating e.g. a primer is applied. This is particularly evident when the primer is applied onto damp concrete where water is gathered in the pores preventing sufficient bonding to the surface.

When all three factors play together there is a high probability of osmosis occurring that can lead to blister formation (see Figure 7).

Figure 7
Osmotic Blistering



The new waterborne curing agent technology offers waterborne high film-build flooring formulations with unique performance properties. The micro porous morphology of the epoxy thermoset network gives heavily filled formulations the ability to “breathe” over substrates with high moisture vapor transmission – a major factor in blistering of conventional epoxy floors. Proper selection of primer and topcoat for the waterborne self-leveling floor does not limit the passage of moisture vapor but enhances adhesion and chemical resistance.

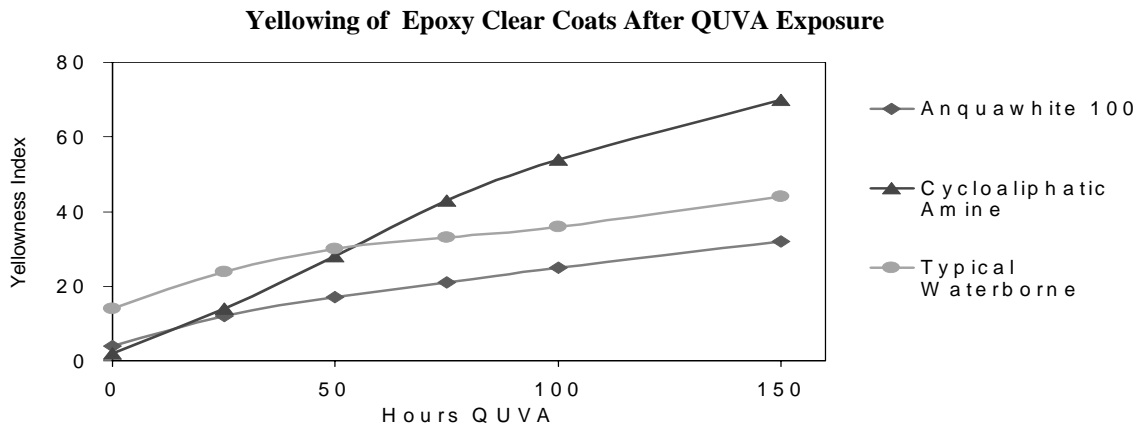
New Technology 3: Stain Resistance against Acidic Foods

This new amine functional polymer dispersed in water and propylene glycol methyl ether, is designed for use with either liquid epoxy resin or solid epoxy dispersions in two component water borne epoxy coatings and to provide excellent food stain resistance. In addition, it offers low yellowing and good water resistance (see formulations in Tables 7 and 8).

Yellowing Resistance

This new curing agent for waterborne epoxy systems exhibits a low initial color that allows the formulation of transparent or white top coatings. It also offers better color stability than other waterborne systems or 100% solids formulations as demonstrated in the graph below. Yellowing resistance can be further improved by using excess epoxy in the formulation.

Figure 8
Osmotic Blistering



Chemical and Stain Resistance

The chemical resistance and spot resistance were benchmarked against established water-based epoxy technology. Good solvent resistance is observed in many water-based systems. However, this new curing agent offers marked improvements in acid resistance.

Table 5

Chemical spot resistance 1h and 18h exposure

	<i>New Curing Agent</i>		<i>Waterborne A</i>		<i>Waterborne B</i>	
	1h	18h	1h	18h	1h	18h
Toluene	+	+	+	+	+	+
Ethanol	+	+	+	+	+	+
Sulphuric acid (10%)	+	+	+	+	H	B
Acetic acid (3%)	+	+	H	B	H	B
Acetic acid (10%)	H/B	B	B	B	B	B

+ =no change; H=haze; B=blisters

Food Stain Resistance 18h Exposure

Coatings based on this new curing agent exhibit markedly better stain resistance against common foodstuffs. Coatings are virtually unaffected after exposure; whereas other water-based systems are significantly attacked (see Table 6 and Photos 1 and 2).

Table 6

Stain Resistance

	<i>New Curing Agent</i>	<i>Waterborne A</i>	<i>Waterborne B</i>
Coffee	no change	slight stain	slight stain
Ketchup	no change	yellow stain	stain/blisters
Mustard	no change	yellow stain	stain/blisters
Red Wine	slight stain	yellow stain	yellow stain

Photo 1

Traditional Waterborne Epoxy

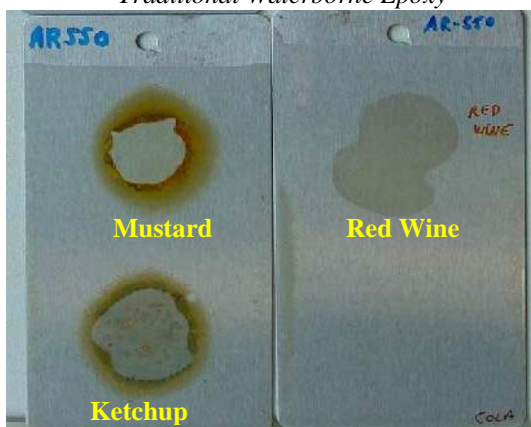


Photo 2

New Curing Agent Technology



Table 7
White Gloss Top-Coat formulation

Component A	
Raw Material	Parts by Weight
Liquid Epoxy Resin (EEW=190)	199.54
Propylene glycol phenyl ether	38.94
Total A	238.48
Component B	
Anquawhite® 100	347.19
Disperbyk® 190	19.47
Surfynol® DF 110D	4.87
Rheolate® 310	9.73
Water	165.47
TiPure® R 706	350.42
Igepal® CO 897	9.73
Surfynol 420	4.87
Total B	911.74
Total A + B	1150.22
Main Characteristics	
PVC	20.8%
VOC (lb/gal)	0.75
VOC (gm/l)	90
Wt Solids	79%
Vol Solids	56%

Table 8
Clear-coat formulation

Component A	
Raw Material	Parts by Weight
Liquid Epoxy (EEW 190)	262.13
Epodil® 748	46.26
Total A Side	308.39
Component B	
Anquawhite® 100	543.85
DI H2O	33.55
Surfynol® DF 110D	4.19
Surfynol® 420	1.05
Total B Side	582.64
Total A + B	891.04
Main Characteristics	
PVC	0
VOC (lb/gal)	0.31
Wt Solids	69%
Vol Solids	67%

Summary

New technologies in waterborne epoxy curing agents are constantly being developed to address not only environmental and worker safety regulations, but also to provide unique technical solutions to overcome well known problems that have challenged our industry for many years. These new curing agents provide practical solutions for adhesion to green concrete, water permeable epoxy self-leveling floors that resist blistering even in problem-prone installation areas, and good stain resistance against acidic foods.

References

1. Walker, F.H., Everett, K.E., Kamat, S., Proc XXII Waterborne, High Solids & Powder Ctngs Symp., 1995, 88.
2. Walker, F.H.; Shaffer, O.; in Provder, T. (ed.), Film Formation in Waterborne Coatings, ACS Symposium Series #648, Washington D.C., 1996, pp. 403-417.
3. Walker, F.H. and Cook, M.I., "Two Component Waterborne Epoxy Coatings," ACS Symposium Series 663 Technology for Waterborne Coatings J. Edward Glass Editor, 1997 The American Chemical Society.
4. A. Arcozzi, R. Arietti, R. Bongiovanni, M. Pocciola, A. Priola; *Surface Coatings International* 1995 (4), 140-143
5. Cook, M.I., "Formulating novel aqueous epoxy resin systems for metal primer applications", 6th Nürnberg Congress April 2001.
6. Wegmann, A., "Waterborne two component epoxy/amine coating systems (part 1)", *Polymer Paint Colour Journal*, 1996, Volume 186, Issue 4384, page 18.
7. Wegmann, A., "Waterborne two component epoxy/amine coating systems (part 2)", *Polymer Paint Colour Journal*, 1996, Volume 186, Issue 4385, page 30.
8. Pye, P. W., Warlow, W. J., "Osmosis as a Cause of Blistering of In Situ Resin Flooring on Wet Concrete," *Magazine of Concrete Research*, September, 1978.
9. Lohe, M., Cook, M.I., Klippstein, A., Lucas, P. A., "Waterborne Epoxy Floor Formulations Address Two Problem Areas – High Moisture Vapor Transmission and Adhesion to Green Concrete"