New Developments in
2K Waterborne Epoxy Coatings

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ABSTRACT

Waterborne epoxy coatings have gained wide acceptance as environmentally friendly alternatives to solvent borne and solvent free epoxy systems. Initially, their growth was driven by the desire to reduce the emission of organic solvents in metal protection and predominantly in industrial flooring applications. Today, waterborne epoxy system provides unique technical solutions to well known problems in the industry and expanding into new application areas.

The paper highlights waterborne epoxy curing agents that provide competitive advantages over conventional systems such as primers and coatings with superior adhesion, particularly on damp concrete, and water vapor permeable systems to avoid osmotic blistering. Model formulations based on these unique curing agents, typical properties and their applications are described.

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.

New developments in waterborne epoxy curing agent technology will be described. At this time, their adoptions 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, thermal shock resistance, rapid development of hardness even at lower temperature, blistering promoted by osmotic pressure.

New Technology 1
One curing agent for 3 different applications: Adhesion over Green Concrete; Deep Penetrating Primer and Thermal Shock Resistant Floor

A) 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 formulation (table 2) was evaluated over two concrete formulations. A 27 N/mm^2 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 and a mild shot blast after three days.

Table 1
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 and Mild 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 after 24 hours. The third slab was allowed to set for three days prior to mild shot blasting then immediately coated with the primer formulation.

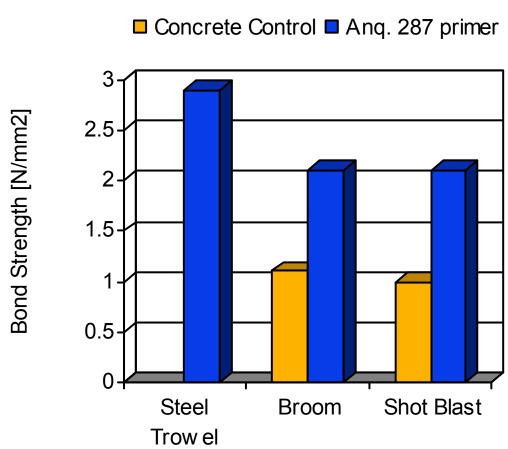
The primer formulation was then checked for adhesion over green concrete, and as a curing compound membrane according to ASTM C309-C.

A-1) Results over green concrete

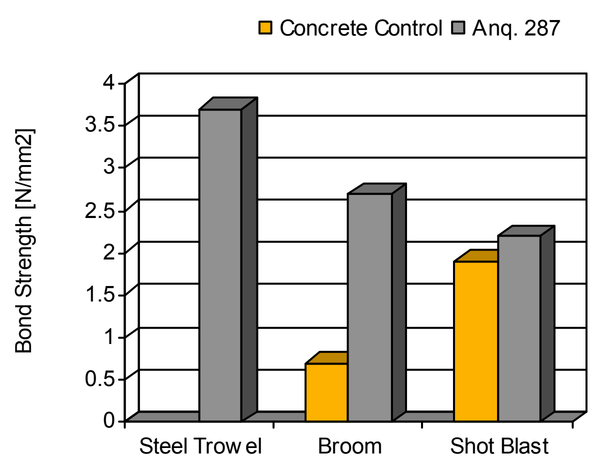
Primer Adhesion: Adhesion strength and mode failure as measure by the dolly pull-off test is shown in Figures 1 and 2, for 7 and 30 day cures, respectively. As can be seen, the steel trowel finished concrete gave higher strength than broom and shot-blasted surfaces. In all cases, the bond strength over primed concrete was greater than over the unprimed concrete. In all cases adhesion was greater than 1.7 N/mm^2, 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 1

Bond Strength after 7 and 30 days cure

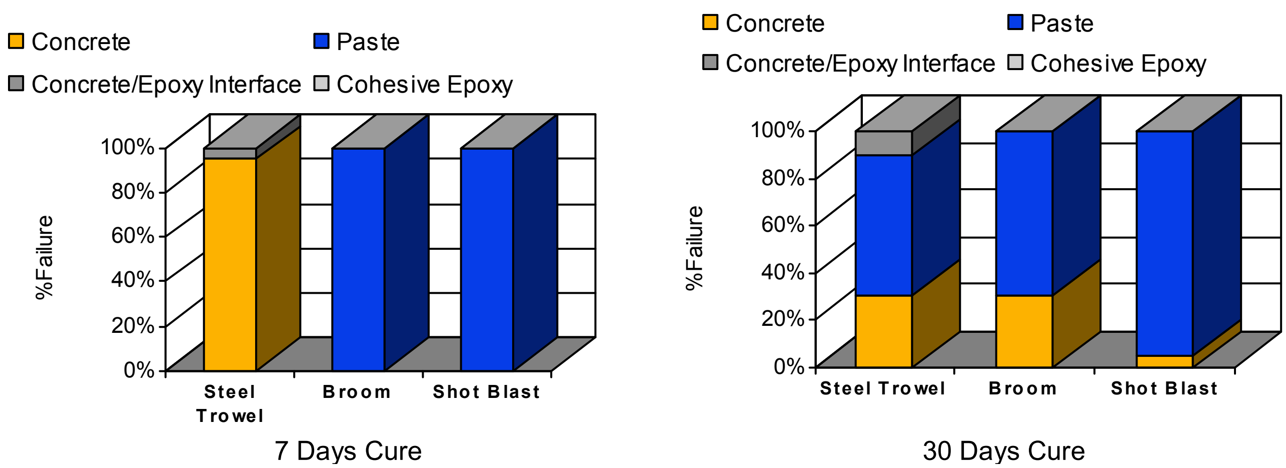


7 Days Cure



30 Days Cure

Figure 2
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 2
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

B) Thermal shock resistant and Fast hardness development floor

This novel curing agent can be used with liquid epoxy resin and cement containing aggregates to formulate self levelling grade or trowel grade flooring. Key advantages of such formulations are:

- Rapid development of hardness even at lower temperature.
- Good workability and easy clean up
- Excellent moisture permeability compared to typical cementitious urethane-based flooring
- Good surface appearance
- Good chemical resistance
- Good thermal shock resistance
- Good hot oil resistance

Following is a starting point * formulation for self leveling floors.

		By wt.	By %	Supplier
A side	Liquid Epoxy Resin (EEW = 190)	22.0	13.7	Various
B side	Anquamine 287 curing agent	27.7	17.2	Air Products
C side	Type I white portland cement	22.5	14.0	Various
	Fine aggregate (~30 mesh)	59.0	36.6	U.S. Silica® #2 Q-ROK®
	Medium aggregate (~20 mesh)	12.0	7.5	U.S. Silica® #3 Q-ROK®
	Course aggregate (~16 mesh)	17.8	11.1	U.S. Silica® #4 Q-ROK®

* The starting point formulation can be further optimized to achieve desired handling and physical properties by using accelerating or retarding agents as well as adjusting the aggregate blend, adjusting the water to cement ratio, and using flow control additives.

Thoroughly mix A and B sides to make an emulsion, then slowly add C side while mixing to ensure the aggregate blend is thoroughly mixed and completely wetted.

The starting point formulation was tested for key handling and performance properties including hardness development, chemical resistance, thermal shock resistance, and moisture vapour permeability.

B-1) Hardness Development

The formulation presented at table 2, demonstrates excellent hardness development with foot traffic allowable on the floor in as little as 4 hr. This is a 50% reduction compared to standard cementitious urethane based flooring. The ultimate compressive strength of the this formulation is 33 N/mm^2 compared to 34.4 N/mm^2 for the standard urethane based flooring.

	1 hr	2 hr	3 hr	4 hr	6 hr	8 hr	24 hr
Shore D @ 25°C	0	30	40	60	65	70	70
Shore D @ 10°C	-	-	-	-	-	-	65
Shore D @ 5°C	-	-	-	-	-	-	60

B-2) Chemical Resistance

A chemical resistance study was performed using a standard spot test method and a standard immersion test method, ASTM D 1308.

Spot test: The following products/chemicals were placed on a sample of the starting point formulation after a 7 day cure. The chemicals were covered by watch glass. After twenty-four hours at 21˚C, the exposed area was examined for physical damage.

Products/Chemical	Observation
Mustard	No damage to the exposed surface
Ketchup	No damage to the exposed surface
Lactic acid	No damage to the exposed surface
Vinegar	No damage to the exposed surface
Lemon juice	No damage to the exposed surface

Immersion test: Samples of the starting point formulation after a 7 day cure were immersed in the following chemicals for twenty-four hours at 21˚C. The samples were removed from the chemical bath and tested for hardness with no recovery period.

Products/Chemical	Hardness, Shore D
Initial	82
10% acetic acid	60
30% nitric acid	75
Sodium hypochloride	80
60% perchloric acid	78

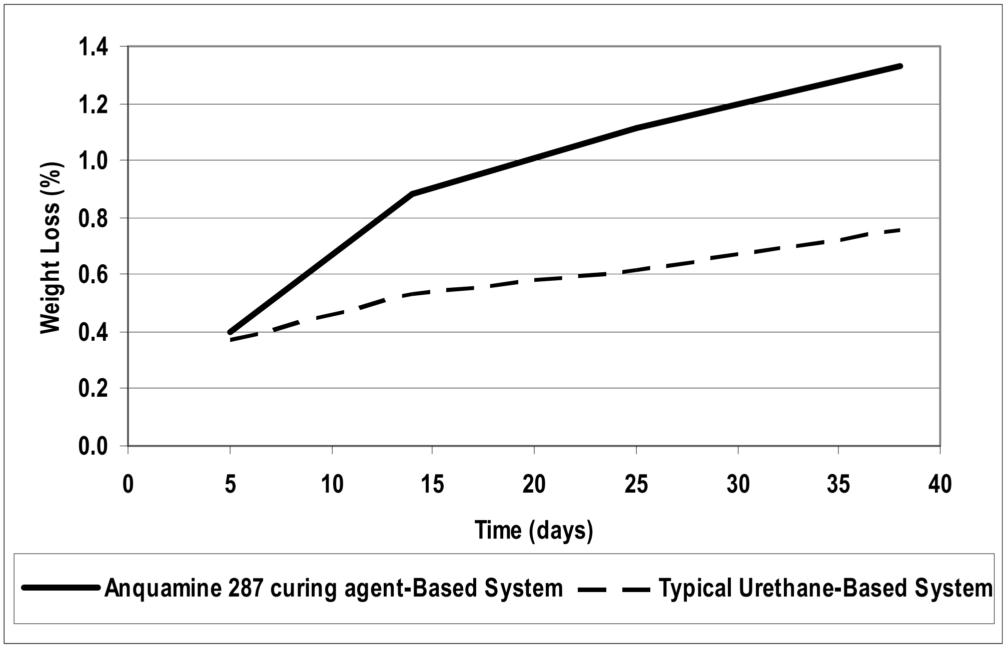
B-3) Thermal Shock Resistance

To evaluate the effect of rapid changes in the surface temperature of this cementitious epoxy flooring system and to evaluate the effect of steam exposure, the starting point formulation was applied to a thickness of 3/8" on concrete blocks. After seven days cure, the blocks were held at 5˚C for 15 hours and then immediately exposed to 100˚C water. This cycle was repeated four times. The blocks were then held at 5˚C for 15 hours and then immediately exposed to steam for 5 minutes. After the thermal cycles and steam exposure, the surfaces were examined for cracks or any other damage. The bond strength of the exposed areas was tested by ASTM C1583-04. The bond strength was 3.4 N/mm^2 (substrate failure) before and after the thermal shock test protocol. There was no damage to the exposed surface observed. A commercially available cementitious urethane based formulation was also tested with identical results.

Additionally, hot cooking oil at 220C was placed in a pool on the surface of the sample and allowed to cool to room temperature. The bond strength was 3.4 N/mm^2 (substrate failure) before and after the hot cooking oil exposure. There was no damage to the exposed surface observed.

B-4) Water Vapor Permeability

Following the ASTM E96 -95 test method (wet cup), accelerated moisture vapor permeability was tested at 40˚C. For this test, 3/8" thick samples were used following a 7 day cure. The following chart shows that the new curing agent has better permeability than typical cementitious urethane-based system.



C) Deep penetrating primer

A deep penetrating primer for concrete can also be formulated with this new curing agent and a starting point formulation is for such application is:

	Parts by Weight
Liquid Epoxy Resin (EEW=190)	80
Anquamine 287 Curing Agent	100
Water	360

To develop the formulation, mix the liquid epoxy resin into the Curing Agent. This will result in a thick emulsion. Mix the emulsion thoroughly, and then add the water slowly in four portions, making sure that each portion is properly incorporated before the next one is added. The primer will now be 24% solids in water

The resulting emulsion can be brushed or rolled onto the concrete. It can also be sprayed or applied with a squeegee. With a very low viscosity of 10 cP, the penetration of this primer is much deeper than standard water based epoxy primer.

The bond strength results (table 3) shown below were obtained after applying the above formulation to old concrete block. When the primer was applied, the block was free of contamination and no additional surface preparation technique was applied.

Table 3
Bond Strength (N/mm^2) to concrete with mode of failure

Primer cure time	Bond strength	Mode of failure
7 days @ 77F	2.8	Substrate failure
30 days @ 77F	2.8	Substrate failure

New Technology 2
Moisture Vapor Transmission

Blistering of synthetic-organic floor 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:

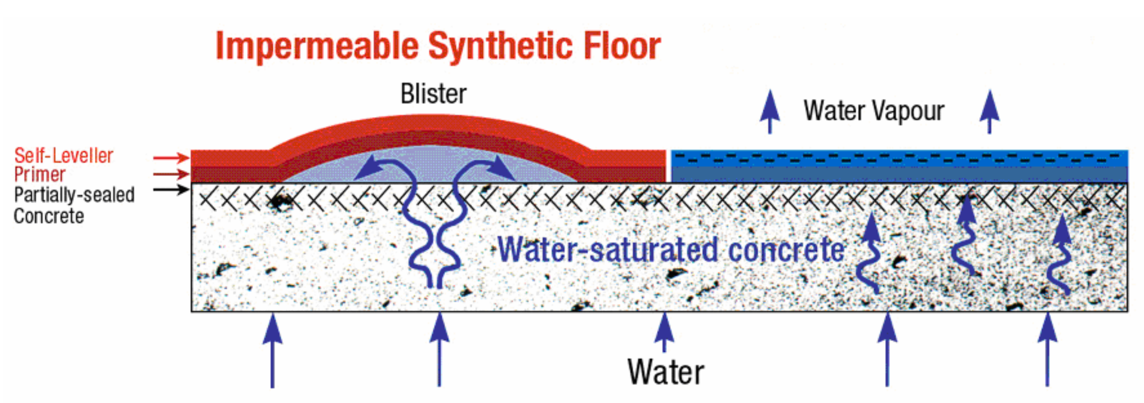
(a) Presence of water (liquid and/or vapor)
(b) Presence of salts or water-soluble organics
(c) Presence of a semi-permeable membrane

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 3).

Figure 3
Osmotic Blistering



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
TiO2 (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

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 "breath" 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
Concrete Primer and Pigmented Concrete Coating

This novel waterborne curing agent technology is designed for use with standard liquid epoxy resin (EEW=190). It is specifically designed for cost effective concrete floor coatings at up to 300 micron applied film thickness and it will easily emulsify standard liquid epoxy resins; the use of emulsifiable resins is not required.

This new waterborne curing agent was developed to deliver the following performance advantages:

- Fast drying times
- Low colour and good yellowing resistance
- Good pigment wetting
- Visible end of pot-life
- Cost effective concrete protection

A) Recommended epoxy resin

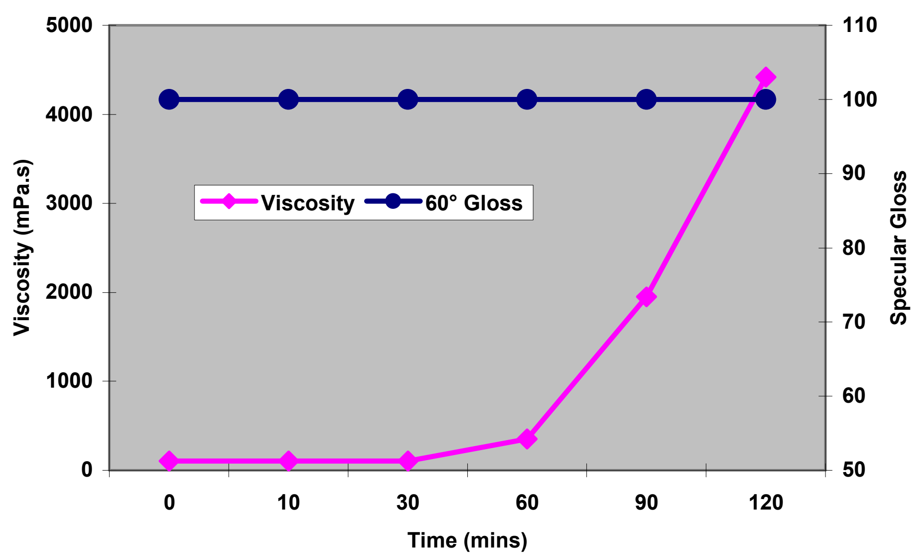
Experimental Curing Agent exhibits good compatibility with standard liquid epoxy resins based on Bisphenol A or F. Reactive diluent modified epoxy resin will offer improved handling and formulating latitude within coating formulations. As with all systems, the inclusion of diluents will retard the hardness development and ultimate hardness of coated films. Resins modified with reactive diluents, such as Epodil® 748 or hexanediol diglycidyl ether, exhibit very good compatibility and produce films of high clarity and gloss. A modification level of approximately 10% to yield a resin viscosity of approx. 2,000mPa.s is ideal to give a good balance of handling and property development

B) Pot-life profile

The viscosity profile (Figure 4) of experimental curing agent exhibits a stable viscosity for at least 60 minutes to yield cured coatings with a high and constant gloss and hardness throughout the pot life. After 60-90 minutes a sharp increase in viscosity represents a visible end of pot-life.

Figure 4

Pot-life profile and Gloss stability



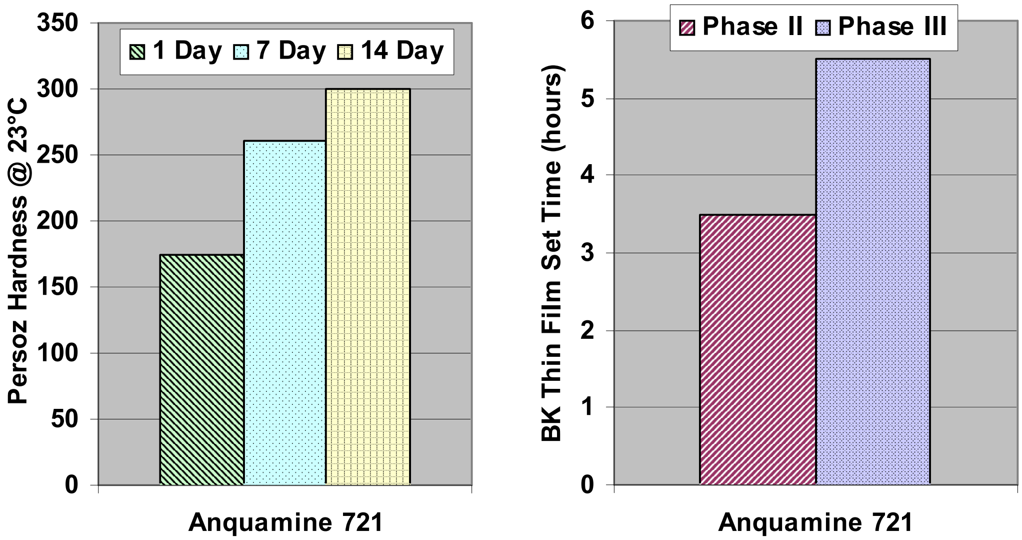
C) Drying time and hardness development

Figure 5 shows the hardness development and Beck Koller, Thin Film Set Times of the new curing agent cured with an unmodified Bisphenol A diglycidyl ether epoxy resin using a mix ratio of 150 PHR. The experimental curing agent yields coatings with an ultimate hardness of approximately 300 as measured by Persoz pendulum hardness with undiluted liquid epoxy resin.

It is recommended to use the new curing agent at advised stoichiometry of 150PHR (EEW=190). It can be used at 10-15% above the recommended loading to accelerate hardness development and increase ultimate hardness by 25% without negatively impacting other properties.

Figure 5

Hardness Development and Dry Speed with Liquid Epoxy Resin



D) Concrete primer

The clear coating, in table 5, is ideal to be used as a concrete primer. It is prepared by taking 60 parts of curing agent and diluting to 40% solids with water. This is then mixed with 40 parts of component B for 2-3 minutes using hand mixing to produce a homogeneous emulsion. Once the emulsion is formed, water is slowly added to give the desired application viscosity and mixed for 1-3 minutes before application. To produce a coating with 40% mixed solids 60 parts of water is required, this will give an initial application viscosity of 100 – 200 mPa.s.

Table 5

Concrete Primer Formulation

			Clear-coat
A-Component			
1. Curing Agent	Anquamine 721	Air Products	60.0
2. Diluent	Water	Local	15.0
B-Component			
3. Epoxy Resin	DER 331	Dow Chemical	40.0
		Sub Total	**115.0**
Mix part A & B until emulsion is homogeneous			
C-Component *- General Primer (40% solids)*			
4. Diluent	Water	Local	**60.0**
After mixing Part A and B, water addition is required to adjust to application viscosity.			

E) Concrete primer: adhesion results

The formulation in table 5 was tested for adhesion over concrete at different conditions, results are shown in table 6.

Table 6

Adhesion on Concrete

	60% Relative humidity						**90% Relative humidity**					
	10°C		23°C		35°C		10°C		23°C		35°C	
	Dry	Damp	Dry	Damp	Dry	Damp	Dry	Damp	Dry	Damp	Dry	Damp
Adhesion on Concrete (N/mm2)	9.1	5.7	8.5	7.1	8.1	7.2	7.7	6.3	10.0	7.2	7.3	5.5

F) Matt Grey Coating Formulation

The grey coating formulation, in table 7, is prepared by mixing Component A with Component B for 2-3 minutes using hand mixing to produce a homogeneous mixture. Once mixed water may be slowly added to give the desired application viscosity and mixed for 1-3 minutes before application. To produce a coating with an initial application viscosity of 300-500 mPa.s, addition of 10 – 15% water is required.
This formulation is ideally suited as a primer or topcoat for concrete floor coatings at 100-300 micron applied film thickness. The highly filled paint provides a cost effective, fast touch dry and good hardness (6H) when cured.

Table 7

Matt Grey Coating Formulation

			Matt Grey Coat
A-Component			
1. Curing agent	Anquamine 721	Air Products	31.00
2. Defoamer	Surfynol DF-62	Air Products	0.25
3. Levelling agent	Surfynol 420	Air Products	0.50
4. Pigment TiO_2	Kronos 2160	Kronos	8.00
5. Pigment	Carbon Black Flamruss 101	Degussa	0.10
6. Pigment	Bayferrox 1420	Bayer	0.40
7. Filler	Blanc Fix Micro	Sachtleben	16.00
8. Filler	Talc 10M2	Luzenac	11.00
9. Matting Agent	Deuteron MK	Deuteron	4.00
10. Diluent	Water	Local	28.75
			100.00
A-Component Manufacture Procedure: • Charge components 1-3 and stir homogeneous at low shear • Slowly add pigment and fillers while increasing speed to 10-20 m/s • Grind with high speed disperser at approx. 10-20 m/s for 15min • Add remaining components at low shear rate. * Some of the water may be added during addition of pigments and fillers to adjust viscosity in order to achieve a uniform grind.			
B-Component			
11. Epoxy resin	DER 331	Dow	**18.00**
12. Reactive Diluent	Epodil 748	Air Products	**2.00**
Total			**120.00**

After mixing Part A and B approximately 10 – 15 parts of water may be required to adjust viscosity for application.

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, thermal shock resistance, cost-effective concrete protection and water permeable epoxy self-leveling floors that resist blistering even in problem-prone installation areas.

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