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3-Dimensional Epoxy Binder Structures for Water Damp Permeable and Breathable Coating and Flooring Systems

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Summary: Blisters and delamination are common problems in the epoxy and polyurethane flooring industry. Main reasons are osmotic effects and hydrostatic water pressure, because of the moister content of fresh concrete. Today's best recommendation is to wait 28 days, combined with perfect surface preparation. Even then, problems can't be excluded when following standard and conventional ways only. The patented technology for water based Emulsion Curing Agent technology enabled water-damp permeable Coating and Flooring systems. After completing the hardening process, this flooring system creates a highly durable micro porous structure, based on a 3D epoxy network. Due to the special nature of the matrix, only water vapour can pass through the system without liquid water penetrating through. This unique system is a perfect extension to conventional epoxy and polyurethane flooring systems. General performance properties, application examples and a description of the polymeric structure of the floor coatings are discussed herein.

Keywords: epoxy resin, polyamines, water based curing agents, crosslinking, microstructure, high performance polymers

Introduction

Concrete Coating and Flooring Systems

When a concrete substrate needs to be protected from environmental attack, there are many different types of coating and flooring technologies that can be used. Examples of these include polyurethanes, methyl methacrylates, polyesters and epoxies. Solvent-free epoxy systems are one of the most versatile technologies employed and are used in a wide variety of applications including primers, floor paints, self levelling, screed and mortar floors. Epoxy binder systems are typically two-component formulations consisting of a liquid epoxy resin and an amine functional curing agent. Epoxy resins are either based on bisphenol-A or bisphenol-F diglycidyl ethers. Their high viscosities require dilution with lower viscosity mono or difunctional reactive diluents.

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In Europe the most commonly amine-curing agents for flooring applications are based on modified cycloaliphatic amines of which isophorone diamine (IPDA), meta-xylylenediamine (MXDA) and bis (p-amino cyclohexyl) methane, (PACM) are the most widely used building blocks. As stand alone curing agents, all of the above amines will only undergo partial cure when mixed with an epoxy resin at ambient temperature. The lack of full cure (B-staging), leads to brittle coatings with poor performance properties. In order to maximise the degree of cross-linking, thus overcoming B-staging, curing agents need to be formulated with non-reactive plasticizers, of which benzyl alcohol is most commonly used within the industry.

Waterborne Epoxy Curing Agent Systems

The first generation of epoxy waterborne curing agents were based on solvent free polyamides and were made water soluble by inclusion of a nonionic surfactant or through salting with an organic acid[1]. The high viscosity and water dilution profile of the polyamides allowed for low solids coating formulations only. Formulated systems tended to have short pot lives and coatings were often high in colour and slow to cure, particularly under condition of low temperature (<10°C) and high humidity (>80%). Higher performance products were subsequently developed and introduced into the market place[2] during the late 1980's and early[3] 1990's. Their chemistry was based on aliphatic amine adducts, which exhibit better colour stability and a higher solids content at the same viscosity compared to earlier polyamide products. The higher solids contents coupled with the fast reactivity inherent in aliphatic amine curing agent has lead to faster dry speed and through cure even under the adverse conditions mentioned above.

A common disadvantage of waterborne epoxy systems is that higher film build coatings, >500μm cannot be readily employed. Their use has been limited to sealers, primers and floor paints[4], where a wet film thickness is in the region 100-200 μm is usually applied. At significantly higher film build, such coating systems may encounter problems with entrapped water being present in the film after full cure. Entrapped water results in a downgrading of the performance properties, resulting in poor surface appearance, loss of gloss or soft films. Cracking (Figure 1) will be observed with typical waterborne curing agents used for self-levelling floor applications.

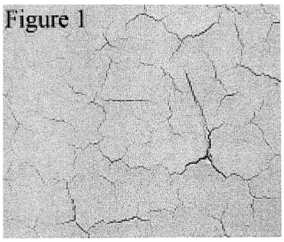


Figure 1

A novel waterborne curing agent technology has been developed[5] to overcome the limitations of previous waterborne epoxy systems. The new Emulsion Curing Agent (EMC) technology is based on a curing agent emulsion of an ultra high molecular weight aliphatic amine-epoxy adduct in water with high amine functionality and can be viewed as the 3rd generation waterborne curing agent for liquid epoxy resin.

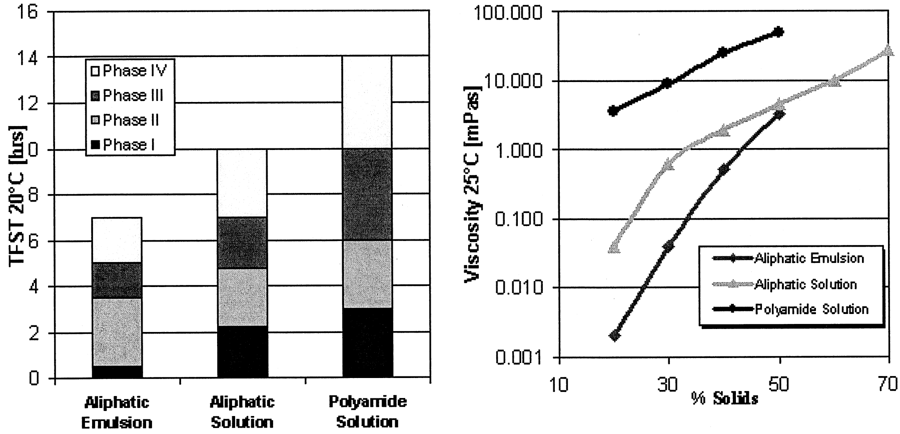
This new technology incorporates three key design features for optimum performance:

(a) Very high compatibility with liquid epoxy resin ensuring good emulsification

(b) Optimised hydrophile-lipophile balance for good emulsion stability and

(c) Removal of unreacted raw materials and by-products, which could reduce performance.

This new aliphatic amine emulsion technology results in coatings that dry significantly faster at ambient temperature. This is clearly demonstrated by comparing the Beckman-Koller thin film set times (phase I-IV), for three types of waterborne curing agent-epoxy coating systems. The aliphatic amine emulsion achieves a hard dry time (phase IV), within 6 hours compared to a hard dry time of 14 hours for a similar coating based on a waterborne polyamide curing agent. The new curing agent technology also exhibits a more effective dilution profile allowing the application of higher solids coatings at the same viscosity



Beck Koller dry times measured on 150 micron wet film clear coats

Figure 2: Dilution Profiles and Drying Times of Waterborne Curing Agents

Waterborne Self-Levelling Floor Formulation

Ease of application combined with optimum mechanical and chemical protection as well as providing easy to clean surfaces has made solvent-free, self-levelling epoxy floors the first choice in concrete protection. Modified solvent free systems using cycloaliphatic curing agents are predominantly used for this type of application and can be viewed as the industry standard. Typically, such protective flooring systems are formulated with low filler to binder ratios (1,5 to 2,6:1), which are deemed necessary in order to ensure good flow and deaerating properties at the point of application.

In order to overturn the old belief that with waterborne technology higher film build coatings cannot be formulated, recent application studies focused on the development of a waterborne self levelling floor using the new generation waterborne curing agent. Development activities successfully lead to the starting point formulation as described in Table 1.

Table 1. Waterborne Self-Levelling Floor Formulation

A-Side:	**Component**	**Supplier**	**Weight (%)**
EmulsionCuring Agent	Epilink® 701	Air Products	11,00
Curing Agent	Anquamine® 401	Air Products	2,50
Defoamer	Byk-045	Byk Chemie	0,70
Pigment TiO_2	Kronos 2160	Kronos Titan	3,80
Diluent	Water	Local	9,10
Filler	Baryte Powder F	Sachtleben	36,00
Filler	Quartz Powder M6	Sibelco	18,00
Filler	Quartz Sand 0,1-0,3 mm	Local	18,50
Thixotropic Agent	Deuteron VT 819 (3% in Water)	Schöner GmbH	0,40
			100,00
B-Side			
Epoxy Resin	Epires® ER8	Air Products	10,00

The significant difference compared to a solvent free cycloaliphatic system is the fact that water can now be used as a diluent to achieve sufficient flow and deareation. This allows for a reduction of the total binder content from approximately 30% in a conventional cycloaliphatic epoxy floor formulation, down to 15% in the waterborne system (Table 2).

This waterborne self-levelling floor contains approximately 15% by weight of water with theoretical volume solids of 70%. The composition would suggest a significant volume reduction to be observed upon evaporation of the water, eventually causing the floor to undergo severe shrinkage leading to cracking. However, upon visual inspection no defects are observed after the system has fully cured.

Table 2. Formulation Properties

	Waterborne Self-Leveller	Cycloaliphatic Self-Leveller
Binder content [%]	15	30
Filler : Binder	4,3 : 1	2,6 : 1
Volume Solids [%]	70,0	99,8
Water Content [wt%]	15,0	0,0

To quantify this observation an experiment was conducted to determine the degree of shrinkage. A specimen of the floor was prepared and cast into a mould of 2,5cm x 2,5cm x 25cm with two metal studs attached to each end. The distance between the studs was measured and used as a reference point. After 24 hrs the cured blocks were removed from the moulds and measurements were taken between the two studs every 24 hrs to determine the degree of shrinkage. The level of shrinkage after 14 days cure is the range of 1,3-1,5%, significantly lower than the maximum theoretical shrinkage of 30%. Most of the water is driven out during the very first day when the bulk part of the shrinkage occurs. Thereafter no significant change is observed as can be seen by the flat profile from day one onwards.

Comparative performance properties of waterborne and cycloaliphatic floors are summarised in Table 3. Flow properties as measured by flow out diameter from a cylindrical container are the same for the two systems. The handling time of the waterborne system at 45 minutes is within the same range as the cycloaliphatic system, as well as offering a comparable final Shore D hardness. Hardness after day one of the waterborne system is in excess of a Shore D value of 65, sufficient for foot traffic.

Bond strengths on shot blasted concrete coated with both the waterborne and solvent free epoxy self-levellers were determined by the dolly pull off method according to DIN 1048. Both systems exhibit bond strengths of >2 N/mm^2 (required minimum value), with a cohesive mode of failure occurring in the concrete substrate.

Abrasion resistance was measured in accordance with ASTM D 5178-91 utilising a Tabor abrasion tester fitted with wheel number C117. Similar weight losses within 1000 cycles are observed with both systems.

The surface finish of the waterborne floor is matte in comparison to the glossy cycloaliphatic finish. While it is the arguable which surface appearance is more attractive, the matte surface appearance of the waterborne floor proves to yield better scratch resistant. Application on uneven substrates also proves to better hide the application/surface differences.

It is anticipated, that the lower binder content in the waterborne floor formulation will affect the mechanical properties of the floor system. Experimental results confirm that the waterborne system exhibits lower compressive as well as flexural strength compared to a cycloaliphatic floor. Normal traffic areas typically require a compressive strength of 20MPa and the strength of the water based epoxy floor (40MPa) exceeds this basic requirement.

Table 3. Basic Performance & Mechanical Properties of Epoxy Self-Leveller Systems

	Waterborne	Cycloaliphatic
Flow out [cm]	15.9	16.5
Handling Time [min]	45	30
Hardness, 7d [Shore D]	80	85
Bond Strength [N/mm^2]	5	3
Abrasion resistance [mg/1000 cycles]	156	138
Surface appearance	Matte	Glossy
Compressive [MPa]	40	62
Tensile [MPa]	5	7
Flexural [MPa]	11	30

Water Vapour Permeability

Water vapour can readily pass through most concrete substrates due to small capillaries. However, when the concrete is coated with a conventional solvent free epoxy floor, the coating will act as a vapour seal and hinder water evaporation from the concrete. Typically, we are dealing with two different types of water transmission problems. One being the hydrostatic water pressure, which is a result of the differential between the highest elevation of a water column and the lowest physical point of a structure and the other being osmotic pressure.

Osmosis is defined as the spontaneous flow of a liquid through a semi-permeable membrane, from a dilute to a more concentrated solution. As a result, the liquid volume of the initially more concentrated solution increases until the hydrostatic pressure generated in its 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. An estimate of the forces that can occur has been described applying the simplified description of osmotic pressure (p) according to Van 't Hoff (Equation 1)

$$p = Dc*R*T \qquad \text{Equation 1}$$

Dc = difference in concentration of soluble salts in mol/l R = gas constant; T = temperature in Kelvin

Assuming a NaCl concentration of 1 mol/l yields a theoretical osmotic pressure of ~2,4MPa. This pressure or higher, at increased salt concentrations is sufficient to exceed the bond strength of the coating to the concrete substrate thus leading to disbondment of the coating.

Three requirements must be fulfilled for osmosis to take place:

(a) Presence of water (liquid and/or vapour)

(b) Presence of soluble salts

(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. The water content also depends on utilized water to cement ratio as well as cure conditions. The principal causes and effects of osmotic blistering for impermeable epoxy coatings on concrete has been extensively studied and reported by other authors[6]. It has been proposed that a higher concentration of soluble salts are present in the top section of the concrete that cannot migrate into the interior of the slab due to a more dense structure present in the bottom section. The difference in soluble salt concentration coupled with concrete permeability for inorganic salts between the top and the bottom section have been identified as major contributors to meet the osmotic cell conditions.

A comparison of how impermeable and permeable epoxy coatings affect blister formation is given in Figure 3.

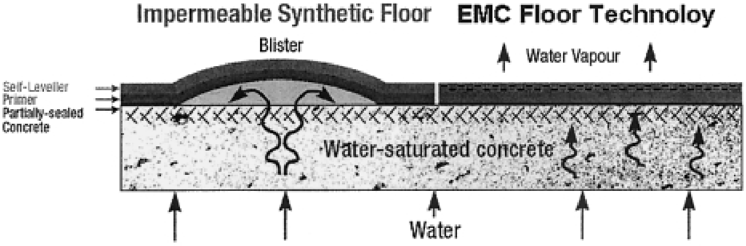


Figure 3: Osmotic Blistering

If pressures are allowed to accumulate and they are not dissipated or relieved by venting; developing pressures exceed the adhesive bond strength to the concrete, thus leading to disbondment from the substrate. Contrarily, permeable coatings are far less susceptible to the effects of these pressures than non-permeable coatings.

Two factors will influence the permeability of a coating. At pigment volume concentrations (PVC) higher than the critical pigment volume concentration (CPVC), the presence of capillary channels in the film causes the water vapour permeability to increase dramatically[7]. It has also been suggested to determine CPVC by measuring water vapour permeability[8]. The other contributing factor is a permeability provided by the nature of the polymer matrix itself. The lack of any substantial shrinkage in the external dimensions of the new waterborne floor as discussed earlier, suggests that the cured polymer matrix forms a micro porous structure. A study of water vapour permeability has therefore been conducted in accordance with DIN 52615 to calculate moisture resistance factor and ASTM E96-95 to calculate permeance comparing the conventional cycloaliphatic and the new waterborne floors[9].

The moisture resistance factor (m) indicates how many times greater the moisture resistance of the material is in comparison with the resistance of a motionless layer of air of the same thickness at the same temperature. The m-factor is a dimensionless quantity, hence is a material specific constant that allows direct comparison of two systems excluding the effect of coating thickness.

Results of the permeability study confirm the hypothesis of a water vapour permeable floor coating, (Table 4). The measured permeability of the waterborne floor is 30 times greater than that of the solvent free floor as expressed by the m-factor.

Coatings are classified as permeable when a U. S. permeability rating of greater than 3 perms* (=$1,7x10^{-7}g/s/m^2/Pa$) is achieved[10]. Standard concrete with a compressive strength of 21 MPa typically exhibits a permeance rating of 20-30 perms. (=$1,1$-$1,5x10^{\square 6}g/s/m^2/Pa$). With the new waterborne system a permeance of 11 perms is readily achieved, which is more than sufficient to comply with this definition of a permeable coating. Typically, cycloaliphatic floor systems do not exhibit the required permeability. This degree of permeability opens up the potential for the waterborne system to be used where osmotic pressure is a known problem.

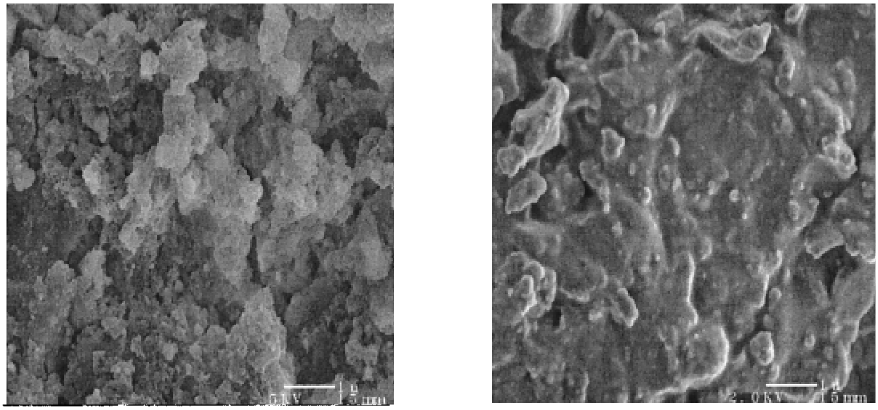
Table 4. Water Vapour Permeability of Epoxy Self-Levelling Floors

	Waterborne	Cycloaliphatic
Film thickness [μm]	2,550	1,870
WVT [$g/m^2/24hrs$]	8,1	0,4
Permeance [perms]	11,7	0,09
Permeance [$g/s/m^2/Pa$]	$6,7 \times 10^{-7}$	$0,05 \times 10^{-7}$
μ-Factor	1,000	30,000

WVT = Water Vapour Transmission

1 perm = 1 grain/hr/ft^2/in Hg

The increased permeability as determined by the above test method is confirmed in scanning electron microscopy (SEM) images on floor castings of the two systems under investigation. The SEM images in Figure 4 show a magnification of 20.000 focused exclusively on the cured epoxy-amine binder system. A marked difference between the waterborne and the solvent free system is evident. A continuous structure with very few voids is observed with the cycloaliphatic thermoset whereas the waterborne system shows a sponge like appearance with voids and channels exhibiting a micro-porous structure that is permeable for water vapour. This analysis suggests that permeability is not only achieved due to a formulation beyond CPVC but that the underlying polymer structure created by the new waterborne curing agent is an integral part of this property. Work has focused on the development of an amine-curing agent that shows applicability in the area of permeable, water based epoxy flooring. This approach can provide the formulator with an additional tool to solve the osmotic blistering problem.



Waterborne Self-Leveller Solvent Free Cycloaliphatic Self Leveller

Figure 4: Comparison of SEM Images (20,000 *x* Magnification)

Additionally, the control of the residual moisture in the concrete would not be viewed as critical, therefore reducing the waiting times prior to application of the protective coating. The epoxy system is also an alternative to the application of polymer modified concrete[11], where the new approach will offer advantages in the area of improved mechanical and chemical properties as well as an improved decorative surface appearance.

Conclusions

The new generation waterborne technology allows the formulation of waterborne high film build coatings with unique performance properties that are complementary to well established solvent free cycloaliphatic curing agent floors. The water vapour permeability of the waterborne self-levelling floor expands the range of applications for epoxy technology, allowing the formulator to apply floors in areas where osmotic blistering has been previously observed. For example, floors below grade, or floors where a damp proof membrane is absent or has started to fail.

Another new dimension in waterborne flooring technology is the development of a matte surface and the absence of amine carbamation. The latter property, allows floor coatings to be applied in colder and more humid conditions than currently possible with conventional solvent free epoxy systems. The additional advantages are high temperature resistance, impact resistance and good chemical resistance. The very low free amine content and the absents of non-reactive plasticisers enable a safer working environment.

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