Novel waterborne 2K Epoxy-Hardener Dispersions with top performance and minimum impact on health & environment

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Summary

The challenge driving the development of modern coating systems is to bridge the gap between ambitious property requirements and increasing environmental concerns. Although this is generally perceived as a contradiction, a new class of waterborne amine hardener dispersions for 2K-epoxy application prove that these two aspects can be reconciled. On metal and mineral substrates modern requirements regarding performance and environment are met. Fast drying and a very user friendly and robust application behavior help to increase the end user's profitability. The hardeners are ultra-low-VOC, contain no free amines and allow for formulations without hazard labeling.

Introduction

Significant progress has been made in improving the performance of waterborne epoxy coatings since they were first introduced to the market. [1] Even so, interest in these systems has not grown as rapidly as might be expected, given the ever stricter regulatory limits on VOC content and the increasing expectation of end users for more sustainable or 'greener' solutions. Thus, users of water-based epoxy coatings were surveyed to determine what specific issues they have with water-based epoxy coating systems.

Interestingly, many of the complaints related to the amine hardeners, and particularly their rheology. Traditional waterborne hardeners have a very high solid content in their form of delivery – 80% is usual – and must be diluted before use. Applicators complain that upon dilution to achieve the desired viscosity for pigmentation (20-30% solids), they face a viscosity increase rather than a decrease when the first quantities of water are added. The phase inversion point is only passed when larger amounts of water are added, and only then does the viscosity begin to drop. In addition, at concentrations less than 25% solids, many hardeners are unstable and phase segregate, causing processing problems. The viscosity profile of waterborne (wb) adduct hardeners is depicted in Figure 1.

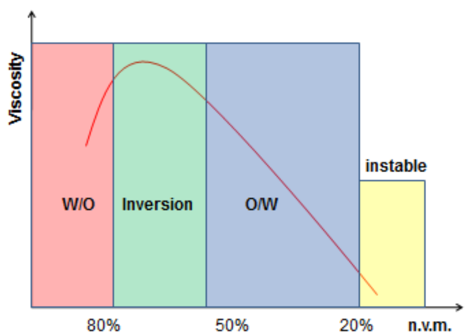


Figure 1: Viscosity profile of water-based adduct hardeners

Users are also concerned about the presence of free amines, which are corrosive substances with a considerable allergenic potential. With waterborne epoxy formulations, it is also a challenge to find the right balance between fast curing and good performance. Good anti-corrosion performance and high chemical resistance is often achieved by compromising the drying speed of a system.

With this information in hand, the development of a new family of amine hardeners for waterborne epoxy coatings was started. The products resulting from these efforts are characterized by a substantially improved ease of use for formulators and applicators compared to standard products and a fast drying behavior which enables the end users to increase the productivity of their processes. The hardeners are ultra-low-VOC, contain no free amines and allow for formulations without hazard labeling.

The specific formulation requirements for metal and concrete substrates made it necessary to develop dedicated products for anti-corrosion applications and applications on mineral substrates respectively.

The System for Metal Substrates

Waterborne epoxy formulations for anticorrosion coatings are usually formulated with epoxy dispersions with a molecular weight of approximately 1000, often referred to as Type 1 dispersions. The reduced crosslinking density compared to formulations with liquid epoxy results in improved elasticity and hence adhesion, which is the prerequisite for satisfactory anticorrosion behavior. The new amine hardener targeting anticorrosion formulations has been developed for the combination with Type 1 dispersions to achieve optimum anti-corrosion performances.

Table 1: Properties of the new hardener for waterborne epoxy anticorrosion formulations

Solids content	~41%
N-H equivalent	~1000 g/mol (fod)
Viscosity	~1000 mPas
Particle size	~100 nm

The product is very user-friendly due to its low viscosity in form of delivery, dilutability to very low solids contents without separation issues, as well as shear and freeze/thaw stability. Unlike many other amine hardeners, it shows good stability with many active anti-corrosion pigments. Therefore the pigmentation can be done in the amine hardener, opening up interesting formulation options.

It is possible to combine the pigmented hardener with different epoxy dispersions to formulate over a wide performance range. The properties of the coating formulation and the applied film can easily be fine-tuned to provide customized performance in terms of flexibility, viscosity, minimum film formation temperature, drying speed and VOC level.

In other words, one pigmented Part A can be combined with different dispersions for specific applications. As shown below in Tables 2 and 3, when using the new hardener and either an unmodified solid epoxy dispersion or a flexibilized dispersion, it is possible to prepare waterborne epoxy coatings that are hard or flexible, respectively. Formulation 1 was used to evaluate the potential of the present system.

Table 2: The new system for anticorrosion coatings

	11.2	Deionized Water
	3.3	Wetting-and dispersing agent
	0.1	Mineral oil-based defoamer
II	8.5	Talcum
	20.5	Titanium dioxide
	0.4	Iron oxide yellow
	1.1	Iron oxide black
	23.1	Barium sulfate
	4.0	Zinc/iron phosphate
	1.35	Zinc phthalate
III	0.05	Mineral oil-based defoamer
	0.6	Hydrophobic ester alcohol
IV	**Mixture of**	
	0.6	Polyurethane thickener
	1.0	Methoxypropanol
V	24.2	Amine dispersion hardener 1
Total	100	**Formulation 1 – Part A**

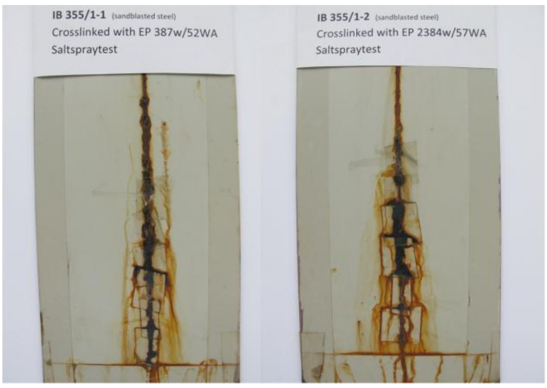
	Higher flexibility		**Faster drying**	
	100.0	Formulation 1 – Part A	100.0	Formulation 1 – Part A
	48.4	Flexibilized solid EP dispersion	36.3	Unmodified solid EP dispersion
	1.6	Deionized Water	3.7	Deionized Water
Total	150.0		140.0	

Table 3: Performance characteristic of Formulation 1

	Higher flexibility	**Faster drying**
Crosslinking ration NH/EP	0.5	0.5
Pigment/Binder	1.6/1	1.9/1
VOC	Approx. 70 g/L	Approx. 40 g/L
Tack free time	3 h	1:45h
Block resistance	after 24 h drying degree 5 [2]	after 24 h drying degree 7 [2]
Pendulum Hardness (König) [3] after 24 h after 7 d	35 s 105 s	75 s 110 s
Flexibility Erichson cupping [4] after 7 d ambient drying	3.0 mm	1.0 mm
Delamination after 1000 h salt spray test [5] Substrate: cold rolled steel; DFT approx. 70 µm	7-9 mm	5-6 mm

With the new hardener the crosslinking ratio can be varied from 0.5-0.75% without affecting the dry time, corrosion resistance, gloss or mechanical properties. Only chemical resistance and hardness development improve as the crosslinking ratio increases.

Most importantly, excellent corrosion resistance is achieved with this fast-drying waterborne epoxy system. Figure 2 shows sandblasted steel panels coated with approximately 100 microns of ambient dried Formulation 1 after a 1000 h saltspray test.



Formulation 1 with flexibilized EP dispersion   Formulation 1 with unmodified EP dispersion

Figure 2: Sandblasted steel panels coated with approx. 100 microns of ambient dried Formulation 1 after a 1000 h saltspray test. [5]

Improved Application Robustness and Productivity

Formulation 1 shows good adhesion to a broad variety of metals and alloys and provides excellent corrosion resistance, even on extremely challenging substrates with variable quality. On insufficiently cleaned, oily cold rolled steel panels, most standard waterborne systems suffer from strong delamination in the saltspray test after a very short time. This strong susceptibility of waterborne epoxy primers to surface contamination has severely limited their use to date. As can be seen in Figure 3, however, significantly less delamination occurs when the new hardener is used.

It should be noted that this gain in application safety should not encourage the applicator to skip proper surface preparation before lacquering. It does, however, mean that imperfections in the cleaning and surface preparation process are less likely to lead to bad surprises. Thus, the present system is very forgiving, which increases ease-of-application as well as the productivity.

1 **2**

Figure 3: Adhesion to oily substrates:
Cold rolled steel panels were treated with a drilling oil emulsion and subsequently wiped with a dry cloth. Lacquer application was achieved with a standard low pressure air spray gun. The panels were dried for 7 d at ambient temperature before exposure to the saltspray test. [5]
1: Standard wb epoxy system after 336 h continuous saltspray test.
2: Formulation 1 combined with unmodified solid EP dispersion after 500 h continuous saltspray test**.**

Furthermore, formulations prepared with the new hardener have very high sagging resistance, enabling the application of much thicker coatings than typically possible with wb epoxy formulations. Formulation 1 can be applied at more than 100 μm DFT in combination with both dispersions without the addition of special mica or smectite-type rheology modifiers. Furthermore, upon addition of 1.5% by weight of a 37% smectite pre-gel, the sagging resistance of Formulation 1 could be increased to approximately 160 μm DFT. In this case, the coating was applied using an airless spray gun (Figure 4)

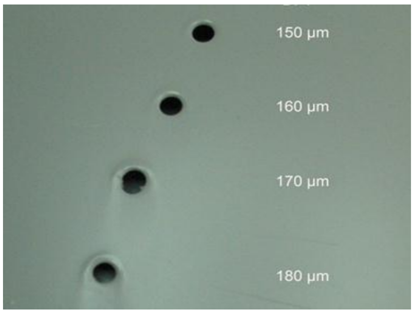


Figure 4: High sagging resistance for thick film builds
Formulation 1 Part A was modified by the addition of 1,5% of a 37% pregel of an organically modified smectite before combination with the unmodified solid epoxy dispersion. Airless spray parameters: 1200 mPas (SR 25 1/s), 0.46 mm valve, 50°; inlet pressure 7 bar ; internal pistol pressure 224 bar.

In addition to its attractive application and performance behavior, considerable productivity gains can be achieved using the new hardener due to its fast drying characteristic. Coatings formulated with the new system can be re-coated in less than 1 hour. In addition, sanding is usually not required due to the very smooth and defect-free film surface that is obtained using the new hardener (Figure 5).

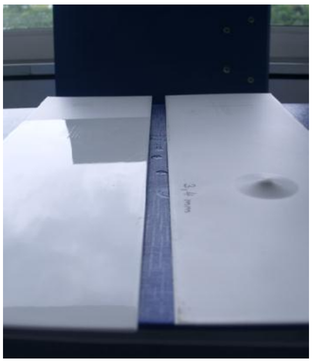


Figure 5: Unmatched Surface Appearance: No Sanding Required
Cold rolled steel panels were coated with Formulation 1 using a standard low pressure air spray gun and dried at ambient temperature. The left panel was topcoated with a waterborne acrylic-isocyanate topcoat. The high gloss and defect free surface of the topcoated panel on the left indicates a very smooth surface of the primer.

The Development for Mineral Substrates

Waterborne epoxy formulations for mineral substrates are very often formulated with reactive diluted liquid epoxy resins with molecular weights of approximately 400 in order to minimize system cost and maximize chemical resistance. Application is done manually, so a reasonably long potlife and a stable performance, especially stable gloss during potlife is needed. As the drying conditions cannot be really controlled in typical concrete applications, a robust drying behavior even under non ideal conditions like low temperature and high humidity is needed. Fast drying to enable two coats per day would have a strong impact on the applicators productivity. The technical route chosen for the metal development – polymeric amine dispersions – let expect some advantages also for concrete applications. The absence of free amines can be noted in the very mild smell of these products, which is a big advantage in the large area applications usually encountered on building sites. Also the allergenic potential of free amines is eliminated by having the amine groups bound to a polymer backbone. The high molecular weight of the new prototype hardeners favors a fast drying behavior.

Compatibility of unmodified liquid epoxy with these waterborne dispersions, high gloss and a stable performance over potlife were clear challenges for this development.

By careful design of the polymer backbone of the hardener a prototype could be developed which meets all the above mentioned criteria. Table 4 shows a grey pigmented formulation (Formulation 2) of amine dispersion hardener 2 which was compared to analogously formulated references (Reference A and Reference B) - two standard wb epoxy hardeners.

Table 4: Amine dispersion hardener for mineral substrates, Formulation 2

I	4.80	Deionized water
	2.60	Dispersing and wetting agent
	0.10	Defoamer
	3.00	Talkum
	8.80	Titanium Dioxide
	5.80	Barium sulfate
	3.20	Ironoxide yellow
	0.80	Ironoxide black
	0.40	Organic Yellow
	0.40	Organic Green
	0.10	Texanol
II	48.00	Amine dispersion hardener 2
Total	**78**	**Formulation 2 – Part A**

	Liquid epoxy resin		**Waterborne epoxy dispersion**	
	78.0	Formulation 2 – Part A	69.8	Formulation 2 – Part A
	16.8	Reactive diluted Type A liquid epoxy resin	59.0	Unmodified solid EP dispersion
	5.2	Deionized Water	2.7	Deionized Water
Total	**100.0**		**131.5**	

Table 5: Performance characteristics of Formulation 2

Solids content	61%	60%
Pigment/Binder ratio	0,6/1	0,6/1
VOC content	20 g/L	20 g/L
Viscosity	1500 mPas	1500 mPas
Tack free time	6h	2,5h
Potlife	1,5h	1h
Pendulum hardness (König) [3] 23°C 50% humidity After 24 h After 7d	65s 130s	98s 115s

Table 5 shows the performance characteristics of Formulation 2 combined with a reactive diluted liquid epoxy resin and a waterborne epoxy dispersion respectively. In the combination with liquid epoxy resin the tack-free time of drawdowns on glass plates could be reduced from >10 h with the reference epoxy hardeners to 6 h with amine dispersion hardener 2. Tack-free time can be further shortened by the use of epoxy dispersions instead of liquid epoxy. It is also worth mentioning that Formulation 2 in combination with the wb epoxy dispersion has a labeling free compound A and B.

While the hardness development at 23°C and 50% humidity of the new system was comparable to the references, the performance at lower temperature and high humidity was clearly superior. Fig. 7 shows the hardness development at 10°C and 85% humidity of the new prototype hardener against reference hardeners 1 and 2. Reference 1 is a hardener with approximately 4 h potlife and a relatively slow hardness development, reference 2 is a fast drying hardener with a potlife of approximately 1,5 h. The new amine dispersion hardener has a potlife of 1,5 h.

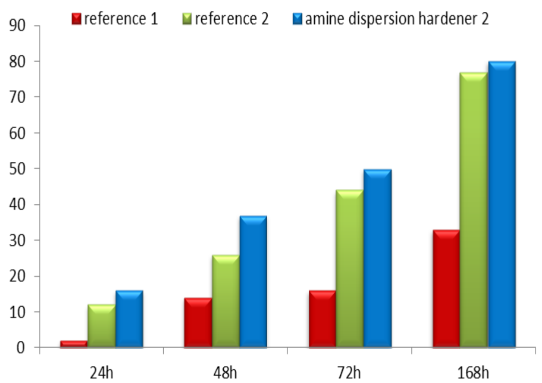


Fig 7: Pendulum hardness development (s) at 10°C and 85% humidity of formulation 2 with amine dispersion hardener 2 and reference hardeners in comparison

Amine dispersion hardener 2 shows very high gloss values of close to 100% at 60° in combination with unmodified liquid epoxy in formulations as characterized in Table 4. The gloss remains stable for 1,5 h.

Water resistance was tested in a 24h immersion test after 7d of room temperature curing. Fig 8 shows the results of the new amine dispersion hardener in comparison to the reference products combined with liquid epoxy resin. The value is a combination of film softening, whitening and adhesion. A value of 0 is very good, 5 is very bad. The new amine dispersion hardener only showed a slight film softening which was reversible, indicating that formulations with higher humidity resistance than usually achieved with waterborne amine hardeners are feasible, which is an unmet need on the market today.

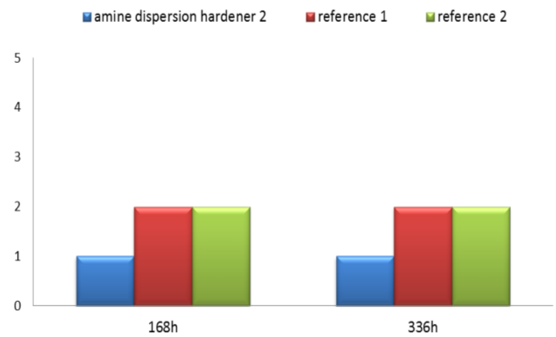


Fig 8: 24 h water immersion test results

The grinding stability of the new prototype hardener was tested by grinding titanium dioxide at different temperatures directly in the hardener on a pearl mill. Up to 50°C no change in viscosity of the resulting paint could be observed. The drawdowns obtained from the respective paints showed the same gloss values regardless of the grinding temperature.

Conclusion

In order to drive greater growth in demand for waterborne epoxy coatings, a new waterborne hardener family has been developed which provides the performance and handling typically associated with solvent-based epoxy coatings, thus addressing the handling and performance issues associated with the current waterborne epoxy coating technology.

The hardeners are free of monomeric amines allowing labeling free and ultra-low VOC formulations for metal and concrete substrates with very mild smell. Applicators can increase their productivity due to the faster drying behavior of the new amine hardeners compared to market benchmarks.

References

[1] Oldring P. et al. Waterborne Solvent Based Epoxies and their End User Applications,Vol.2, *SITA Technology Limited: London, UK*, 1996, Ch. II and IV.
[2] DIN 53150:2002-09
[3] DIN EN ISO 1522
[4] DIN EN ISO 1520
[5] DIN EN ISO 9227