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EPOXY HARDENERS FOR LOW-EMISSION FLOORINGS

High-performance epoxy coatings meet ECO-label requirements. By Christina Cron and Dirk Fuchsmann, Evonik Operations.

The growing demand for sustainable epoxy flooring systems has led to the development of new amine hardeners to meet increasingly stricter regulations. One approach is the use of ultra-low emission hardeners, based on low-viscosity amine building blocks, which contain minimal organic solvents. Water-borne hardeners that avoid organic solvents are also used to reduce the viscosity of the system. Both technologies enable improvements in performance, return to service and surface quality.

Throughout the construction industry, epoxy resins that are cured by amine hardeners are often the favoured options for high-performance, and cost-effective, floor coatings. Application areas range from industrial floorings, for example in the chemical, manufacturing and food industries, to parking decks and warehouses, and also increasingly in non-commercial areas. Given their intrinsic, strong mechanical properties; including high abrasion resistance and excellent chemical resistance, in many cases epoxy systems are generally preferred over the competitive systems like acrylic or polyurethane. Their superior mechanical and chemical stability translate into high durability, and thus a longer service life, enabling end-users to reduce maintenance work and lower downtime costs. By saving on resources and lowering costs, epoxy systems can make a significant contribution to improving the sustainability goals of the construction industry.

In recent years, improving the sustainability of flooring systems has become more and more important, driven by both changes in legislation and increases in market demand. Key focus areas are not only limited to long service life, but also include improved labelling, lower global warming potential, and increased use of bio-based or recycled materials. For flooring applications, low emissions of volatile organic compounds (VOC) are probably the most important aspect, as organic volatiles influence indoor air-quality and therefore the health and well-being of the flooring applicators and the end users of the buildings.

Although amine hardeners for epoxy floorings enable high durability and therefore contribute to this sustainability aspect, some hardeners may still exhibit relatively high VOC emissions. One prominent substance still present in many amine hardeners is benzyl alcohol, which is typically used as a solvent. If applied in poorly ventilated, large indoor areas, emissions from benzyl alcohol, as well as the other ingredients or contami-

RESULTS AT A GLANCE

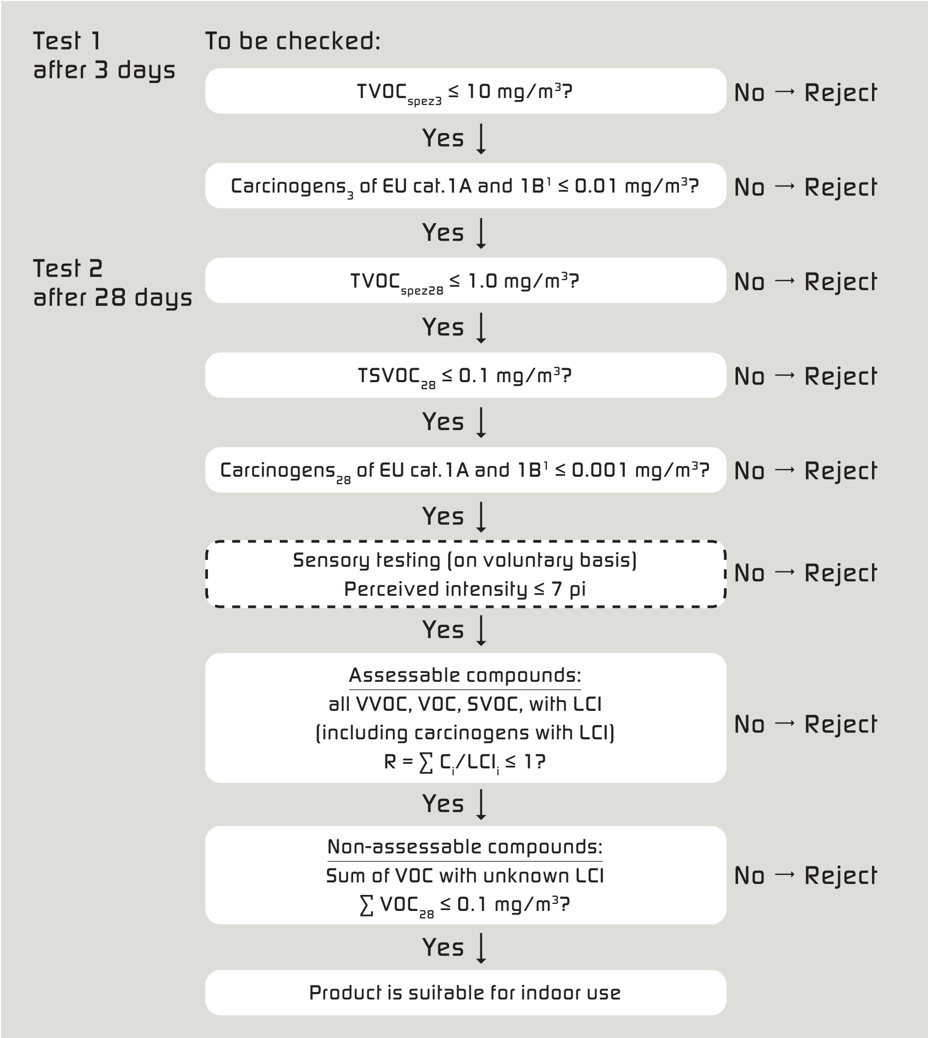
→ Epoxy coatings based on low-emission and water-borne amine hardeners fulfil AGBB and "Emicode" EC 1[Plus] requirements.

→ Water-borne hardeners provide low cost, sustainable alternatives to conventional hardeners.

→ Water-borne and low-emission hardeners both provide high performance, sustainable alternatives to conventional hardeners.

→ Carbon footprints are significantly lowered by the use of water-borne hardeners.

Figure 1: AgBB - Evaluation procedure for VOC emissions from building products; June 2021 – Committee for Health-related Evaluation of Building Products; Germany.



nants with high VOC emissions, can lead to low air quality .

The "Industrial Emission Directive 2010/75/EC" and other tools help to control overall VOC emissions. For the construction sector in Germany, the industry has developed a scoring scheme called AgBB (Ausschuss zur gesundheitlichen Bewertung von Bauprodukten) (*Figure 1*). Another prominent example for an international label focusing on indoor air quality is the "Emicode" label administered by the GEV (Association for Emission-Controlled Installation Materials). Both regulations are widely accepted in the international construction industry to identify products with low VOC emissions.

To reduce VOC emissions and comply with the national and international standards, new technical solutions have been developed. Water-borne hardeners are considered an attractive route towards low-emission epoxy systems as they typically do not contain any organic solvents. An alternative approach are new amine technologies, which allow for 100 % (or at least ultra-high) solid amine formulations due to their low, inherent viscosity (*Table 1*). Compared to the conventional amine hardeners that have been established as the industry standard for many years, both water-borne and 100 % solid hardeners exhibit significantly lower volatile organic content, which is beneficial for occupational safety during the application of a new flooring. However, the most relevant factor is the VOC emission of the epoxy systems, including A and B components that occur after the application, as described in the AgBB and "Emicode" classification systems.

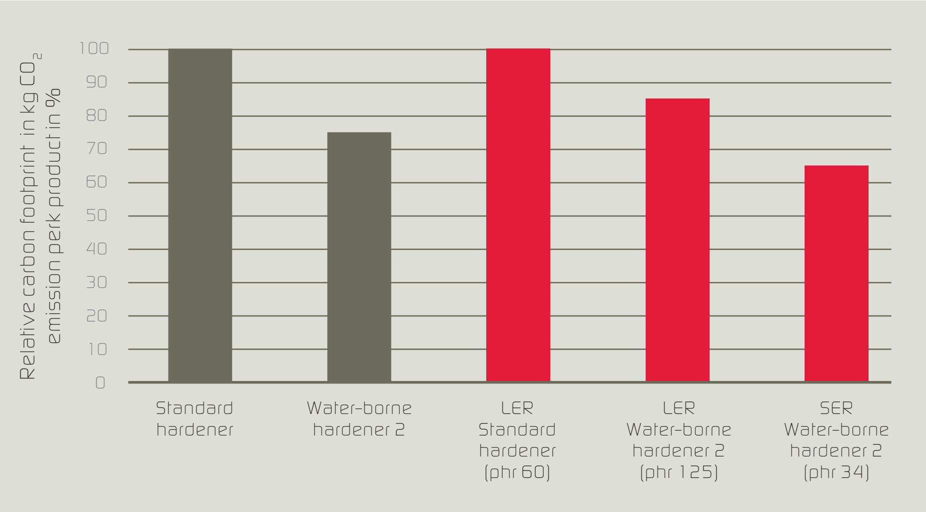
Table 1: Overview of amine hardeners used in emission tests.

	Standard hardener	Ultra-low emission hardener	Water-borne hardener 1	Water-borne hardener 2
VOC content (safety data sheet) according "Directive 2004/42/EC" (... any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101,3 kPa)	25 - 50 %	< 5 %	0 %	0 %
"recommended use level - phr(with epoxy resin EEW 190)"	60	50	160	125
Viscosity in [mPas]	500	500	35.000	8.000

Table 2: "Emicode" classification system.

Limit values in µg/m³	EC1PLUS	EC1	EC2
TVOC after 3 days	≤ 750	≤ 1000	≤ 3000
TVOC after 28 days	≤ 60	≤ 100	≤ 300
TSVOC after 28 days	≤ 40	≤ 50	≤ 100
R value based on German AgBB LCI (NIK) after 28 days	≤ 1	-	-
Sum of non-assessable VOCs	≤ 40	-	-
Formaldehyde after 3 days	≤ 50	≤ 50	≤ 50
Acetaldehyde after 3 days	≤ 50	≤ 50	≤ 50
Sum of formaldehyde and acetaldehyde	≤ 0.05 ppm	≤ 0.05 ppm	≤ 0.05 ppm
Sum of C1A/C1B VOCs after 3 days	≤ 10	≤ 10	≤ 10
Any C1A/C1B VOC after 28 days	≤ 1	≤ 1	≤ 1

Figure 2: Global warming potential (GWP, excluding biogenic carbon) from a cradle-to-gate LCA for the hardeners (B component only, grey) and epoxy systems (A+B components, red).



This paper compares VOC emissions of epoxy floorings based on different amine hardener technologies. For this, the industry standard adduct hardener "Ancamine 1618" will be compared to the water-borne hardeners "Anquamine 721", "Anquamine 728" and the ultra-low emission hardener "Ancamine 2739" (*Table 1*), and the results are assessed according to AgBB and "Emicode". The paper demonstrates the benefits of both water-borne and ultra-low emission hardeners when it comes to emissions from organic compounds as well as the performance of the floor coatings.

AGBB AND "EMICODE" TEST METHODS

The European civil engineering market classification systems offer architects, contractors, and craftsmen guidance to choose materials that ensure maximum safety, certify optimum health protection, and promote high environmental compatibility.
Both AgBB and "Emicode" classification systems are test chamber methods for which emissions are measured after 3 and 28 days in standardized test chambers with defined temperature, air change rate, relative humidity, and air velocity in the test chamber.

"Emicode" is a protected product classification system and its eco label has three different classes; the limit values of each category are shown in *Table 2*. The "Emicode" EC2 label is awarded to products that fulfil the basic requirements and are 'low in emissions'. Products with 'very low emissions' are labelled by "Emicode" EC1 label, with "Emicode" EC1PLUS having even stricter limit values.
The emission tests in this paper were carried out according to the AgBB and "Emicode" method. For this purpose, clearcoats based on a diluted bisphenol A/F epoxy resin and the stochiometric amount of epoxy hardener were applied on a glass plate (200 g/m²) and inserted directly into the emission chamber. After 3 and 28 days, air samples were taken and analysed.

EMISSION AFTER 3 DAYS

After three days, all formulations fulfilled the requirements for an AgBB certification (*Table 3*). Due to the high benzyl alcohol content of the standard adduct hardener used, this formulation only complies with the "Emicode" EC2 requirements, whereas the water-borne and low-emission formulations comply with "Emicode" EC1PLUS. In addition, no cancerogenic substances could be detected in all formulations.

EMISSION AFTER 28 DAYS

The standard hardener used exhibits a high VOC, which is attributed to the benzyl alcohol content. Therefore, it is not compliant with AgBB (R value > 1) and so does not fulfil any "Emicode" classification (TVOC > 300). In contrast, the emissions of the water-borne and low-emission hardeners show a very low level of VOC and are compliant with AGBB and "Emicode" EC1PLUS (*Table 4*).
For water-borne hardeners in particular, the formaldehyde content is often critical, but the emission tests demonstrate that the formaldehyde emissions from both the water-borne hardeners used are so low that both fulfil AgBB and "Emicode" EC1PLUS requirements, and would even fulfil the A+ certification of the French Décret-No. 2011-321 regulation.

PERFORMANCE COMPARISON OF AMINE HARDENERS

Despite their beneficial emission profile, water-bornes are often wrongly associated with higher costs, and lower performance than standard solvent-borne hardeners. However, the latest generation of water-borne hardeners exhibit excellent cure speeds, especially when combined with an aqueous solid epoxy resin (SER) dispersion. While the industry

Table 3: Emission test results after 3 days.

	Emission limits [µg/m³]				Emission results [µg/m³]			
	AgBB	"Emicode" EC 1Plus	"Emicode" EC1	"Emicode" EC2	Standard hardener	Ultra-low emission hardener	Water-borne hardener 1	Water-borne hardener 2
TVOC	≤ 10000	≤ 750	≤ 1000	≤ 3000	2.519	41	141	131
Carcinogens cat. 1A and 1B	≤ 10	≤ 10	≤ 10	≤ 10	not verifiable	not verifiable	not verifiable	not verifiable
Formaldehyde		≤ 50	≤ 50	≤ 50	< 2	< 2	2	13
Acetaldehyde		≤ 50	≤ 50	≤ 50	<2	2	4	3
Sum of formaldehyde and acetaldehyde		≤ 0,05 ppm	≤ 0,05 ppm	≤ 0,05 ppm	< 0,01 ppm	< 0,01 ppm	< 0,01 ppm	0,01 ppm

Table 4: Emission test results after 28 days.

	Emission limits [µg/m³]				Emission results [µg/m³]			
	AgBB	"Emicode" EC 1Plus	"Emicode" EC1	"Emicode" EC2	Standard hardener	Ultra-low emission hardener	Water-borne hardener 1	Water-borne hardener 2
TVOC	≤ 1000	≤ 60	≤ 100	≤ 300	788	< 5	13	< 5
TSVOC	≤ 100	≤ 40	≤ 50	≤ 100	< 5	< 5	< 5	< 5
Carcinogens cat. 1A and 1B	≤ 1	≤ 1	≤ 1	≤ 1	not verifiable	not verifiable	not verifiable	not verifiable
Assesable Compounds - R	≤ 1	≤ 1			1,862	0,000	0,017	0,017
Non-assessable compounds	≤ 100	≤ 40			< 5	< 5	< 5	< 5
Formaldehyde (DIBT parameter)	≤ 120				< 2	< 2	2,09	3,91

standard hardener used cures within 20 hours at 10 °C (as determined by TFST measurements), with water-borne hardener 2 and the water-borne resin used a walk-on time of 4 hours at 10 °C can be achieved at a comparable pot life. In addition, the aqueous hardener exhibits excellent adhesion to concrete and high surface qualities.
For a better comparison of the performance the starting viscosity of the formulations have been adapted to the same level by diluting the water-based formulation with water. Overall, this demonstrates that water-borne hardeners cannot only be sustainable alternatives to well-established hardeners containing benzyl alcohol, but they can also help to save resources and lower costs due to higher cure speeds and increased efficiency (*Table 5*).

PRODUCT CARBON FOOTPRINT

Besides VOC emissions, another important sustainability aspect are greenhouse gas emissions, which are often referred to as the carbon footprint. To determine the carbon footprint, a cradle-to-gate life cycle assessment (LCA) was conducted following the principles of ISO 14040/44 and ISO 14067. The calculation is based on primary data for the production process. Secondary data from different databases, and supplier or literature data was utilized for external processes and raw materials. Modelling was performed using the software "GaBi 10" (Sphera Solutions GmbH).
For both the standard hardener and the water-borne hardener 2, major part of both products' carbon footprint (PCF) stems from the raw materials they are made from. Electricity, process steam, and cooling water at the respective production site only has a minor impact on the total PCF.
The PCF of water-borne hardener 2 was found to be ca. 25 % lower than the one for 1618. One significant contributing factor is the comparably high carbon footprint of benzyl alcohol in the standard hardener compared to the fresh water used as a solvent alternative in the water-borne hardener 2.
The lower PCF of water-borne hardener 2 is not only reflected in the hardener itself, but also in the clear coat epoxy formulation as shown in *Figure 2*. When using a standard bisphenol A liquid resin, the carbon footprint of the system can be reduced by ca. 15 % when switching the hardener component from the standard hardener to the water-borne hardener 2. The effect is even more pronounced when using an aqueous solid epoxy resin dispersion that allows for ca. 35 % reduction compared to the industry standard liquid epoxy resin (LER) with the standard hardener.

OUTLOOK

Both water-borne, and ultra-low emission hardeners exhibit significantly reduced VOC emissions of epoxy systems in thin films and comply with the AgBB and "Emicode" EC-1PLUS classification. The assessment in this paper was done for clear coats, used as model systems that only contained epoxy resin as an A component, and the amine hardener as ➜

Table 5: Performance comparison of different hardeners.

Epoxy resin	**Diluted bisphenol A/F epoxy resin**				**Solid epoxy resin dispersion "Ancarez" AR 555**
Hardener	Standard hardener	Ultra-low emission hardener	Water-borne hardener 1	Water-borne hardener 2	
Formulation viscosity in [mPas]	550 - 700				
Thin Film Set Time - phase III at 23°C in [hours]	10	11	9	7	2
Pendulum hardness - Persoz 1d/7d 23°C	145/290	110/280	30/270	60/280	200/280
Carbamation resistance* 1d 23°C	5	5	5	5	5
Thin Film Set Time - phase III at 10°C in [hours]	> 24	> 24	20	9	4
Pendulum hardness - Persoz 1d/7d 10°C	20/140	20/150	10/150	20/160	90/250
Carbamation resistance* 1d 10°C	1	4	2	2	4

* Carbamation resistance following wet patch method (ISO 2812), Scale 1-5 (5=best)

a B component. Future measurements will have to focus on more complex floor coating formulations, including fillers and various additives, as they are expected to contribute to the VOC emissions as well. This will help to generate more practical examples.

In addition to VOC emissions, the product carbon footprint of the standard adduct hardener and a selected water-borne hardener were calculated by a cradle-to-gate life cycle analysis. The production of the water-borne hardener 2 exhibits lower global warming potential than the industry standard hardener.

Future product development of amine hardeners will focus on further reductions of VOC emissions, as well as improvements in the product carbon footprint. For instance, one of the key raw materials in the standard hardener is isophorone diamine (IPD), which is recently now also commercially available as "Vestamin IPD eCO" and made using renewable carbon based on a mass balance approach and is ISCC PLUS-certified [3]. Use of renewable raw materials like this will enable further improvements of sustainable amine hardeners for epoxy floorings in the future.

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