EUROPEAN COATINGS journal

www.european-coatings.com

05 – 2021

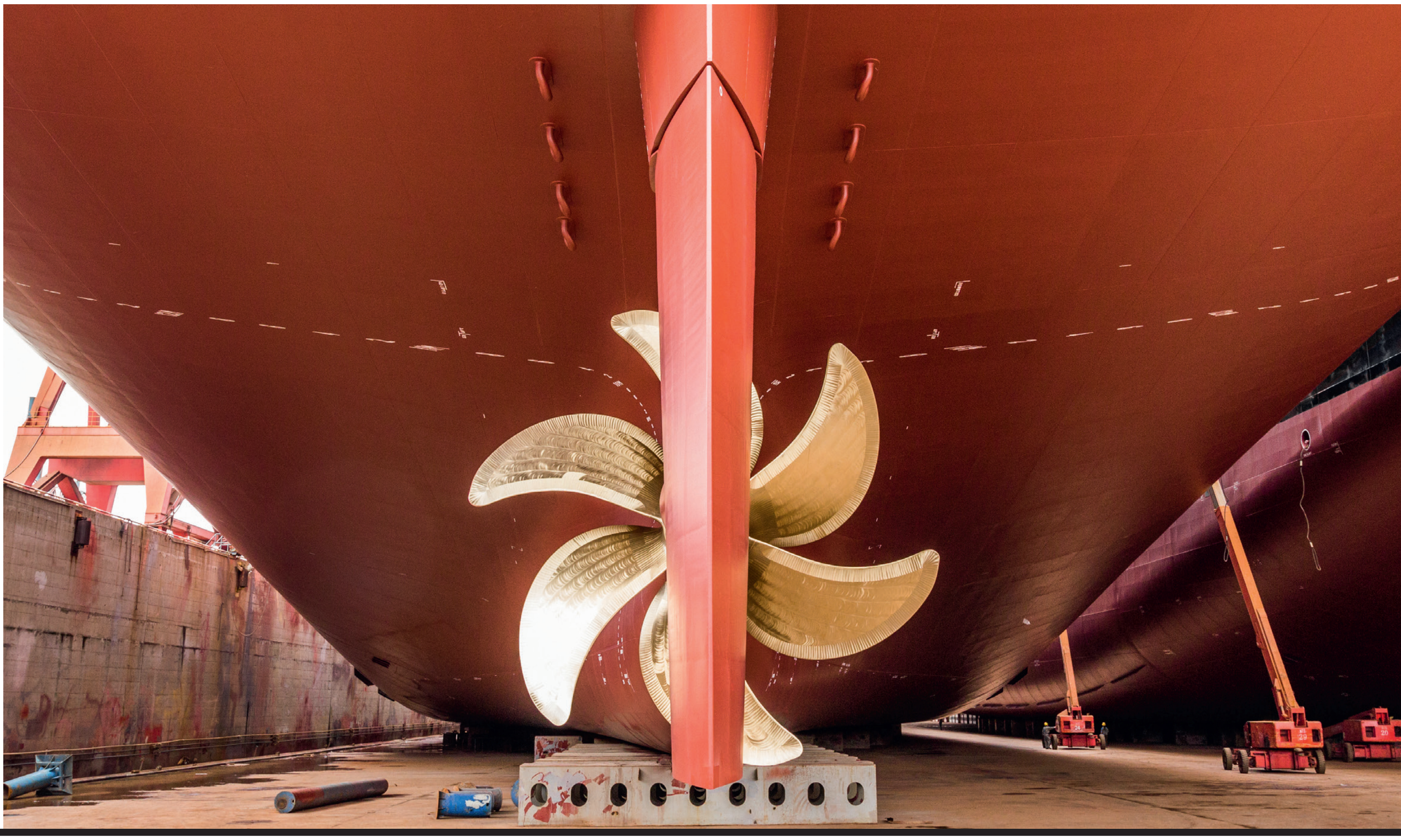
ULTRA LOW EMISSION COATINGS

By Dr Zuhal Tuncay, Evonik Operations

Source: Dirk Peddinghaus - stock.adobe.com

VINCENTZ

Source: Angelika Bentin - stock.adobe.com



ULTRA LOW EMISSION COATINGS

New amine curing agents meet strict VOC regulations and exhibit robust performance during service life. By Dr Zuhal Tuncay, Evonik Operations.

Environmental regulations have increased in the marine and protective coatings industries worldwide in recent years. Current worker safety and environmental protection regulations are among the most important drivers in new product development for epoxy coatings, targeting the reduction or elimination of volatile organic compounds (VOCs).

However, reducing or eliminating the raw materials that would produce VOCs, like solvents and plasticisers in coatings, presents major technical challenges (*Figure 1*) [1]. Requirements for application properties for low VOC coatings, including low mix viscosity, short drying times and long pot life, all in a wide range of climatic conditions, must be achieved without compromising anticorrosive and mechanical properties. This major challenge is driving innovative formulation and new technological developments in curing agent chemistry, such as ours targeting a new class of amine curing agent, allowing epoxy coating formulators to design ultra-low VOC coatings that meet the challenging environmental regulations yet retain high performance during service life. The definition for VOC varies between different regions and directives. Therefore, knowing where the coating will be used is important when referring to VOC level. According to EC Directive 1999/13/EC (Solvent Emissions Directive), a VOC is an organic compound having a vapour pressure of 0.01 kPa at 20 °C and a boiling point in the range of 215-220 °C. The EU "Paint Directive" 2004/42/EC defines VOC as an organic compound having an initial boiling point lower than or equal to 250 °C at an atmospheric pressure of 101.3 kPa. A similar definition is used by the European Eco-Labelling scheme (2002/739/EC amending 1999/10/EC) for paints and varnishes, where the VOC is defined as an organic compound with a boiling point lower than or equal to 250 °C.

KEEPING UP WITH THE REGULATIONS

Within the European Union the broadest instrument for VOC control is the Industrial Emission Directive 2010/75/EU followed by the Decorative Paints Directive 2004/42/EC. Beyond these, national regulations like AgBB in Germany, Belgian VOC regulation and A+ VOC regulation in France set quality standards and foster the development of low-emission products.

Consequently, development towards high-solid coating for preventing metal corrosion is now prevalent. To keep the viscosity of the paint formulation manageable, while minimising solvent demand, curing

RESULTS AT A GLANCE

→ New amine curing agents meet stringent emissions regulations for metal protection in marine and protective coating applications without compromising handling or anticorrosive properties.

→ These agents go beyond very low viscosity and contain little or no plasticisers, adding high compatibility with epoxy resins and good surface appearance after curing.

→ Due to the absence of plasticiser, the new curing agents will deliver high performance during the service life.

→ Good property balance – low viscosity, long pot-life, fast dry time and high flexibility – makes the new technology a suitable replacement for existing high-solid epoxy systems.

agents and epoxy resins with lower initial viscosity are chosen. This negatively affects pot-life, dry time, adhesion and flexibility in the coatings [2].
Typically plasticisers are used to ensure through cure and avoid vitrification in the crosslinking reaction with high-solid systems. This can improve compatibility, dry speed and adhesion, while reducing the initial viscosity. However, plasticisers can leach out of the coating under certain conditions with the coating becoming brittle during the service life, which of course causes cracking over time. Furthermore, under the definition of VOCs in most directives, benzyl alcohol falls within it [3], which limits the use of this raw material for high-solid systems.
Therefore we have a market need for ultra-low or zero-emission coating formulations with robust performance during the service life that also offer a good balance of pot-life, dry time, viscosity and flexibility. To address these needs, we have developed a proprietary new cycloaliphatic amine technology for both polyamide and cycloaliphatic curing agents [4].

NEW PRODUCTS WITH EXCELLENT PROPERTIES

To meet stringent emissions regulations we have developed two new products. They provide properties and performance comparable to typical hardeners based on cycloaliphatic amines or their corresponding adducts. Both products exhibit very low viscosity, with "An-

Figure 1: Overview of state-of-the-art epoxy coatings in comparison to newly developed curing agents [1].

>400 g/l	<250 g/l	0 g/l < x <100 g/l
VOC		
Solvent-borne epoxy coating Resin: SER Amine: Polyamides	**High-solid epoxy coating** Resin: LER Amine: Cycloaliphatic adducts and Mannich bases	**Ultra low or zero VOC epoxy coating** Resin: LER Amine: New curing agents
Pros: - High flexibility - Fast drying and long pot life (6 h) - Long overcoatibility - Remains tacky at low temperature	Pros: - Low VOC - Low temperatrue cure with good apperance - High chemical resistance	Additional value of new cycloaliphatic types: - Real through cure without plasticisers - Performance sustainability over sevice life
Contras: - High VOC - Moderate chemical resistance	Contras: - Long dry time and short pot life (1 h) - Needs plasticizer for fully cure - Moderate flexibility	Additional value of new polyamide types: - High compatibility with LER and zero induction time - Good wetting of the surface

camine 2739" containing ultra-low levels of plasticisers and "Ancamine 2712M" using no liquid plasticisers at all.

While the first has been designed to allow for a longer working life (1.5 h), the second was formulated to provide coating systems with improved blush and carbamation resistance at low application temperatures (≤10 °C), offering improved performance over existing cycloaliphatic amine systems. The base handling and performance properties, including gel time, cure speed and hardness development of clear coatings based on our products compared with a modified cycloaliphatic amine curing agent are highlighted in *Table 1*.

Both products have been formulated to provide a 50 phr loading with a standard liquid epoxy resin (LER). The unique advantage of the two products is the low mixed application viscosity, which is achieved at <10 g/l VOC, whereas the standard cycloaliphatic has a VOC of 160 g/l due to the presence of benzyl alcohol. Additionally, the new curing agents exhibit fast dry speed with equal or better carbamation resistance. The barrier properties of the clear coats have been investigated by electrochemical impedance spectroscopy (EIS), where in all cases pore resistance (Rp) was above 10^8 Ω's obtained following 24 h of exposure to an aqueous salt solution, indicating excellent all-round corrosion resistance.

To ensure a through cure without vitrification of the crosslinking reaction, we investigated degree of curing over time by differential scanning calorimetry (DSC). The data was obtained after allowing the clear coat (DFT 125 µm), consisting of curing agents along with Bisphenol A/F epoxy resin containing an aliphatic epoxy diluent (Epodil 748), to cure for 8 h, 24 h and 7 days. *Figure 2* illustrates the degree of cure as determined by DSC with a heat ramp of 10 °C/min [5]. The results show that the two new products exhibit rapid conversion with epoxy resin to almost full cure (>98 %) at ambient temperature within 7 days without the need for high levels of plasticiser.

To explore the durability of the cured coatings, two additional sets of clear coat panels were prepared using the same formulations based on Bisphenol A/F epoxy resin containing an aliphatic epoxy diluent (Epodil 748, EEW=190, η=900 mPa.s). The first set was allowed to cure for 7 days at ambient temperature and the second set was cured for an additional 2 hours at 150 °C in a fan-assisted oven. We measured the glass transition temperature (Tg) via DSC and the crosshatch adhesion regarding ASTM D3359. In all cases, the Tg of the first set was around 55°C, whereas the second set had a significantly higher Tg for the cycloaliphatic amine (110°C). Also, the crosshatch adhesion of the cycloaliphatic amine-based coating was negatively impacted by the additional heating in the second set. For the crosshatch test the first set is rated as class 5B and the second set as 3B. This suggests that plasticisers are released from the coating during service-life, with the consequent risk of stress accumulation and loss of adhesion. In comparison, our coatings based on two new products did not show any such performance deterioration.

ULTRA-LOW EMISSIONS

Based on the concept of 'lowest concentration of interest' (LCI), defined by the European Commission as a critical emission level for a single component reported in µg/m3, which affects indoor air quality for inhabitants and users during long-term continuous use, the AgBB committee has set an interpretation scheme. This scheme validates the accumulated emission products at 3, 7 and 28 days after applying a coating in indoor applications rated according to EN-ISO 16000 with the following definitions:

VOC: Volatile organic component ranging between C_6-C_{16}

TVOC: Total VOC, accumulated VOC of products ≥ 5 µg/m³ ranging between C_6-C_{16}

SVOC: Slow-volatile organic component > C_{16}-C_{22}

ΣSVOC: Total SVOC, accumulated SVOC of products ≥ 5 µg/m³ with > C_{16}-C_{22}

To establish the emission levels of these new curing agents, we submitted a formulation based on "Ancamine 2739" (Formulation 3, *Table 5*) for emissions testing following the AgBB protocol. The first measurement was performed 3 days after application and cured at 23°C and 50 % relative humidity (RH). *Figure 3* shows less than 1 % emis-

Figure 2: Degree of cure for curing agents in combination with modified LER.

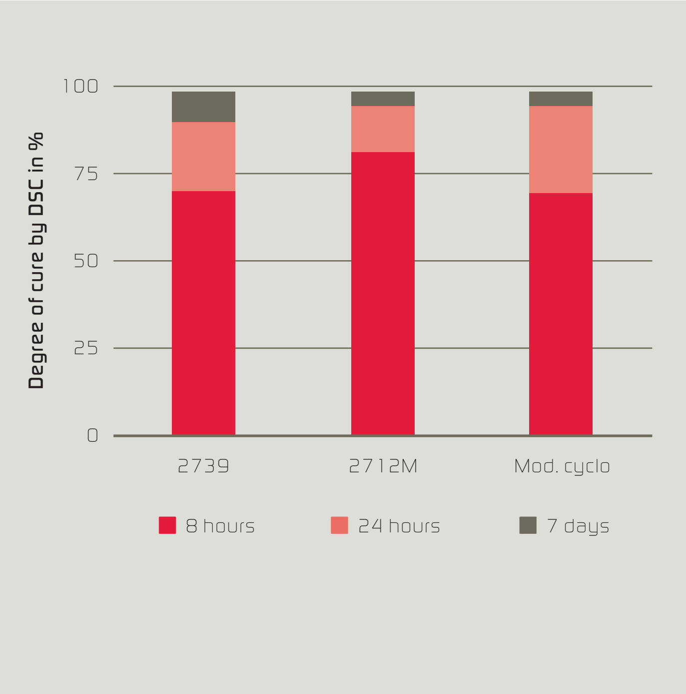
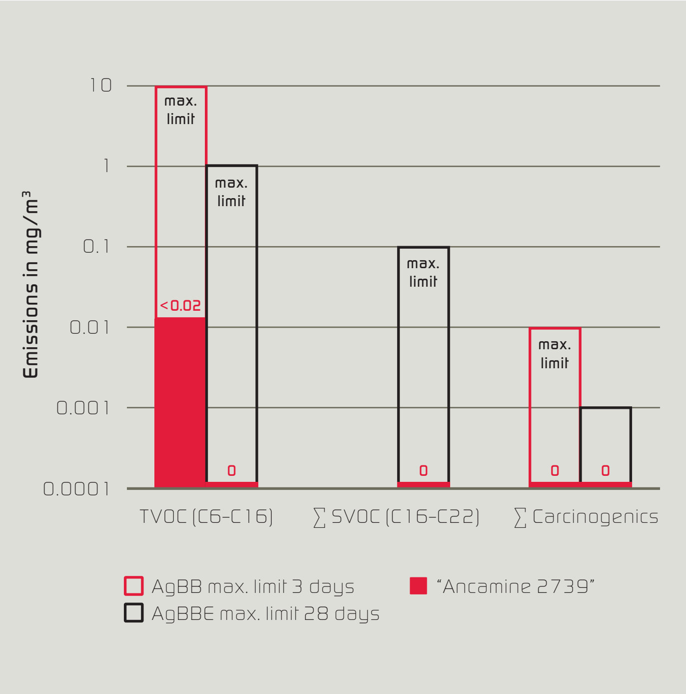


Figure 3: Emission testing results for Formulation 3 based on Ancamine 2739 curing agent following the AgBB testing scheme.



sion of VOC components of the maximum norm and no detection of SVOC or carcinogenic substances. As a result of this extremely low emission, a second measurement was performed after 7 days' cure, demonstrating extremely low emissions; no detection of VOC, SVOC or carcinogenic substances. These results clearly demonstrate that coatings based on our new curing agent ("Ancamine 2739") exceed the AgBB criteria and can be categorised as an ultra-low emission coating system.

HIGH PERFORMANCE OF ANTI-CORROSIVE PRIMERS

Anti-corrosive primers were formulated based on "Ancamine 2739", "Ancamine 2712M" and a modified cycloaliphatic amine utilising the model formulation 1 and 2 in *Table 4*. The general performance properties are summarised in *Table 2* [6].
The general performance properties of the anti-corrosive primers based on "Ancamine 2739" and "Ancamine 2712M" are excellent.

Table 1: Performance properties of new developed curing agents vs modified cycloaliphatic amine.

Property	Unit	"Ancamine 2739"	"Ancamine 2712M"	Mod. cyclo
AHEW	g/eqv	95	95	95
Viscosity at 23 °C	mPa.s	350-650	300-600	300-600
Mixed viscosity at 23 °C	mPa.s	630	850	800
Gel time 150g mix, at 23 °C	min	75	35	40
TFST, phase III, 23 °C	h	9.5	7	8
TFST, phase III, 10 °C	h	17	14	20
Persoz hardness, 23 °C [1 d/7 d]		185/300	240/360	175/315
Persoz hardness, 10 °C [2 d/7 d]		75/200	135/375	60/125
Carbamation resistance 23 °C, 24 h/10 °C,2d		5/3	5/4	5/3
EIS (Rp)	Ω 24h	$1.0x10^{10}$	$2.3x10^{10}$	$9.3x10^{8}$
VOC for system	g/l	10	0	160

All formulations tested with bisphenol A/F resin, C12-C14-glycidyl ether diluted, EEW=190, n=900 mPa.s

Table 2: Performance properties of anti-corrosive primers based on formulations 1 and 2.

Property		Unit	"Ancamine 2739"	"Ancamine 2712M"	Mod. cyclo
VOC		g/l	88	60	160
Persoz hardness	d1 d7	s s	-	202 289	92 161
Impact test (direct)	d7	Kg.cm	-	40	65
Gloss	60°	-	90	103	102
Thin film set time (BK)	phase III	h	8.0	6.5	7.5
Thumb twist drying time	DTT DH	h h	- 9.5	4.0 8.0	4.8 9.0
Cross hatch adhesion[1]	d7	D3359	5B	5B	5B
Salt spray[2]	1500/2000 h		10/10	10/-	10/-
				No scribe creep or field blisters	
Cleveland humidity	1000 h		10	10	10
Pull off adhesion test[3]		MPa	5	/	/

[1] "ASTM D3359" – rating 5 = excellent, no loss of adhesion
[2] Panels were scribed and evaluated for field blisters using ASTM B117. Evaluation of scribe creep was rated in accordance with "ASTM D1654".
[3] Spray applies on sandblasted steel with a DFT of 150 µm

Figure 4: Anti-corrosive primer system based on "Ancamine 2739" after accelerated weathering and pull-off adhesion test.

They provide fast dry as measured by the thumb twist method, corresponding to 9.5 h and 8 h for "Ancamine 2739" and "Ancamine 2712M", respectively, which is comparable to the standard modified cycloaliphatic amine. Due to the absence of plasticisers, these coatings also exhibit improved Persoz hardness development, while maintaining good flexibility. All the coatings provided excellent adhesion to sandblasted steel (SA 2.5) as well as demonstrating excellent salt spray and Cleveland humidity resistance. The cohesive failure by pull-off test further shows the good adhesion.

ZERO-EMISSION POLYAMIDE CURING AGENTS

In addition to cycloaliphatic type amine curing agents, the new technology allows for the design of non- solvent based polyamide curing agents. These offer much higher flexibility with a longer re-coat window than cycloaliphatic amines, showing many benefits compared

Table 3: Comparison of a bisphenol-A epoxy resin – clear coats at 10°C, 23°C and 60 % RH.

Curing agent	Viscosity in mPa.s	Induction time in min	Gloss at 60° at 23°C	Gloss at 60° at 10°C	Flexibility* in mm -pass
Conventional HS polyamide	15000	30-60	81	53	5
Modified polyamide	3000	0	80	68	20
"Ancamide 2769"	150	0	100	94	20

* (Erichsen mandrel test)

Table 4: Anti-corrosive primer start point formulation 1 (F1) based on "Ancamine 2712M" or modified cycloaliphatic curing agents and formulation 2 (F2) based on "Ancamine 2739".

Component A		Parts for F1	Parts for F2	Component B	Parts
Epoxy resin	EEW (190)	31.4	29.2	Curing agent formulation 1	17.5
"Epodil 742"	Reactive diluents	3.6	3.3	Curing agent formulation 2	16.3
"ZetaSperse 2100"	Dispersing agent	1.0	-		
"Tego Aires 900"	Defoamer	1.0	1.3		
"Tego Wet 270"	Wetting agents	-	1.3		
"Bayferrox 130M"	Pigment	5.0	4.7		
"Plastorit 000"	Filler	15.0	28.9		
"Sachtleben micro"	Filler	26.0	-		
"Blanc fixe micro"	Filler	-	18.6		
"Heucophos ZCP-plus"	Anti-corrosive pigment	6.7	-		
"Halox SZP-391"		-	6.2		
"10 ES Wollastocoat"	Filler	10.0	-		
"Bentone SD-2"	Rheology modifier	0.3	0.2		
Xylene/Butanol 4:1	Solvent	1.5	6.3		

Notes:

I. Xylene/Butanol added to achieve application viscosity of ~ 1000 mPa.s

II. Total PVC for formulation 1 = 30 %

III. Formulation1 based on "Ancamine 2712M": VOC = 60g/l, vol. solids = 91.5 %

IV. Formulation1 based on mod. cycloaliphatic: VOC = 160 g/l; vol. solids = 81 %

V. Total PVC for formulation 2 = 29 %

VI. Formulation 2 based on "Ancamine 2739": VOC = 88 g/l, vol. solids = 86.4

to state-of-the-art polyamides. The new "Ancamide 2769" exhibits extremely low initial viscosity, while containing no plasticisers or solvents, and offers improved resin compatibility without the need for further modification, which is reflected by the high gloss in cured coatings [7]. Due to its good compatibility with LER no induction time is needed to achieve good surface appearance and good surface wetting can be ensured. Even at lower temperatures tack- and blush-free surfaces can be obtained. *Table 3* compares clear coats based on this product versus a number of commercial polyamides.
Anticorrosive primer formulations based on this polyamide having a VOC of 85 g/l and a 2 h pot-life exhibit excellent corrosion resistance with minimal or no failures up to 2,000 h in salt spray and prohesion tests. Furthermore, the primer shows very good adhesion even on poorly prepared, rusted substrates, where the pull-off test indicated 6 MPa strength [1].

THE NEXT STEP

The ambition of this study was to create sustainable solutions across all coating areas, but especially in marine and protective applications, where environmental regulations can be the most demanding. We developed an innovative curing agent technology allowing to reduce or even eliminate VOCs in paint formulations, which minimises workers' exposure to hazardous chemicals during application of the coating.
Focusing on workers safety and environmental regulation, this work demonstrated that the new amine curing agent technology can provide ultra-low or zero emission epoxy coating formulations with high corrosion resistance. It has been shown that, due to the absence of non-reactive plasticiser, the coating is more thermally stable and will retain high performance during service life. This will extend the service life of structures and equipments, which additionally reduces their overall impact on the environment. The handling attributes including the low viscosity, long pot-life, fast dry time and high flexibility highlights the applicability of this technology as a suitable replacement for existing high solid epoxy systems.
With the same ambition, we are working on expanding this technology to robust ultra-low emission systems for "winter cure", where the application temperature could drop down to 0 °C.

REFERENCES

[1] M. Cook, Raising the Barrier for marine paints, European Coating Journal, pp. 38-47, 09 2019.
[2] C. Hare, Protective Coatings – Fundamentals of Chemistry and Composition, Pittsburgh, Technology Publishing Company, 1994, pp. 1; 199; 210; 398-400.
[3] The Paint Directive, 2004/42/EC.
[4] Vedage, G., Raymond, W., Cook, M., Rasing, R, Benzylated polyalkylene polyamines and uses thereof, Patent US8147964B2, 2012.
[5] M. Wacker, P. Trawiel und G. W. Ehrenstein, Härtung von Reaktionsharzen Time-Temperature-Transition-Diagramm, Nürnberg: Sonderdrucke.
[6] "Ancamine 2712M" and "Ancamine 2739", Evonik technical datasheet.
[7] Totev, D., Vedage, G., Raymond, W., Rufo, M., Cook, M., „High Performance Polyamide Curing Agents Offering Low Emissions and Long-Term Performance, SLF Congress, Helsinki, 2012.

Dr Zuhal Tuncay
Evonik
zuhal.tuncay@evonik.com

Table 5: Start point formulation based on "Ancamine 2739" prepared for emission test.

Component A	Parts	Component B	Part s
Bis A/F epoxy resin, "Epodil 748" diluted, "EEW 195", n 900 mPas	21.0	"Ancamine 2739"	10.0
Defoamer	0.2		
Levelling agents	0.2		
"Kronos 2160" (titanium dioxide)	4.0		
"Elftex 415" (carbon black)	0.1		
Blanc fixe micro (Filler)	19.2		
Quartz	45.3		