



RAISING THE BARRIER FOR MARINE PAINTS

Driving higher-performance emissions-compliant epoxy systems for long-term asset protection. By Dr Michael Cook, Evonik Corporation.

New developments in the marine and protective coating sectors are being driven by stringent emissions regulations and a growing need for more robust technologies. Given that the binder system is key in determining the final properties and performance of such coatings, it is essential to choose the right resin and curing agent.

Within the coatings market, all geographical regions are looking to provide technology which addresses emerging environmental concerns, with a specific focus on eliminating hazardous raw materials and lowering solvent emissions. Epoxy coatings used in marine and protective coatings are based on epoxy resins predominantly derived from bisphenol diglycidyl ether and are cured with a range of amine hardeners [1] designed to optimally balance handling and end-use performance properties. With the introduction of maximum VOC limits in coating applications, development work has shifted from traditional solid epoxy resins (SERs) to systems based on the lower-viscosity liquid epoxy resins (LERs). LERs enable formulators to achieve higher coating solids ($\geq 80\%$) than the traditional solvent-borne SER systems, where solids are typically

50%. For high-solids systems, reaction kinetics studies show that the pot-life is adversely affected and the drying time extended when coatings are applied to the substrate. The latter effect is due to the polymeric network's having to crosslink and build up sufficient molecular weight to reach the gel point or dry-to-touch state, whereas SER systems are already classed as high-molecular polymers, and dry-to-touch or lacquer dry is observed as soon as the solvents evaporate from the coating film [2]. The epoxy resin and amine curing agent form the coating's binder and determine most of the end-properties [3]. *Table 1* highlights the key differences between conventional solvent-borne and high-solids coatings.

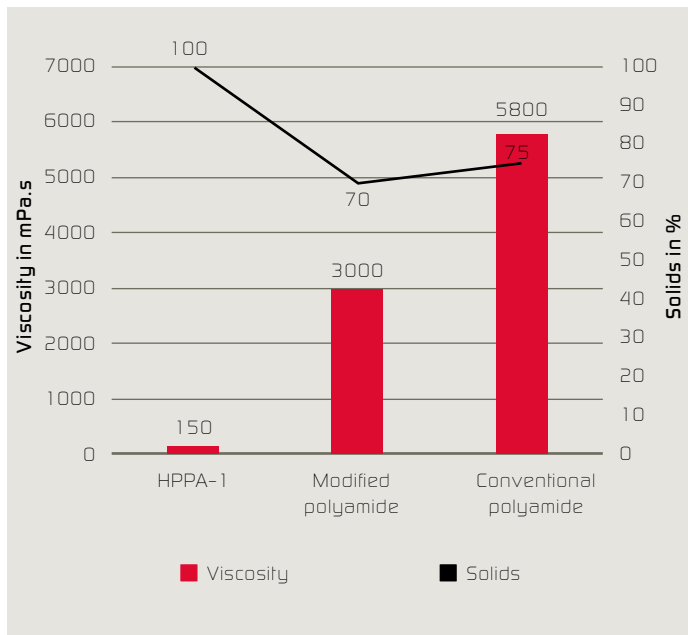
GENERAL DISCUSSION

In the marine and protective epoxy coating sectors, formulators already use a range of curing agent technologies. The chemistry is matched to the end-performance requirements and ensures that the finished cured coating is fit for purpose. In addition, the choice of curing agent also depends on the handling and application properties specified by both the applicator and the asset owner. Polyamides

RESULTS AT A GLANCE

- The correct choice of resin and curing agent is essential for marine and protective coatings.
- In epoxy coatings, a well-designed curing agent will yield systems that offer an very good balance of pot-life, drying rate, viscosity, and flexibility.
- The new amine technology described here can be formulated into 100 % solids curing agents that exhibit low viscosity and need little to no plasticiser for full cure at ambient temperature.
- The coatings are more likely to maintain their properties and performance throughout their service life.
- Very good compatibility with different epoxy resins reduces the tendency to blush, yields a good surface appearance, eliminates induction time and supports multi-component spray equipment.

Figure 1: Viscosity vs solids profile.



are the most popular technology for heavy-duty metal protection [4]. Their long-chain, fatty-acid backbone offers a good combination of corrosion resistance, flexibility and adhesion to a range of metallic substrates. However, polyamide curing agents are often high in viscosity and confer limited solvent and chemical resistance. Polyamides also provide very good pot-life, allowing applicators to continue

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- spray application for up to 6 hours when used with solvent-borne solid epoxy resin. This normally yields low-solids coating formulations that have a VOC content > 400 g/l. Since both the resin and the curing agent have a high molecular weight, the film will rapidly lacquer-dry once the solvent evaporates and it can be safely handled without damage several hours after the initial application.

MULTIPLE CHALLENGES

Formulators face multiple challenges when developing epoxy coatings that have to comply with emerging environmental and performance targets. These include achieving a low application viscosity, coupled with a pot-life that facilitates application by means of conventional

spray equipment. To keep the viscosity manageable, yet minimise solvent demand, formulators must employ curing agents and an epoxy resin of lower inherent viscosity. In practice, this means total or partial replacement of the polyamides and the solid epoxy resins with lower-molecular technologies, such as aliphatic or cycloaliphatic amine-based curing agents, which are then used in conjunction with a combination of liquid epoxy resin and epoxy-functional diluents. The general benefits and limitations of the different types of curing agent are summarised in *Table 2*.

Using different chemistries in the formulation of high-solids epoxy coatings brings several performance benefits. Many cycloaliphatic systems can now deliver improved low-temperature cure, as these curing agents react faster, and are more compatible, with LERs than with polyamides.

Figure 2: Mix viscosity vs solids profile.

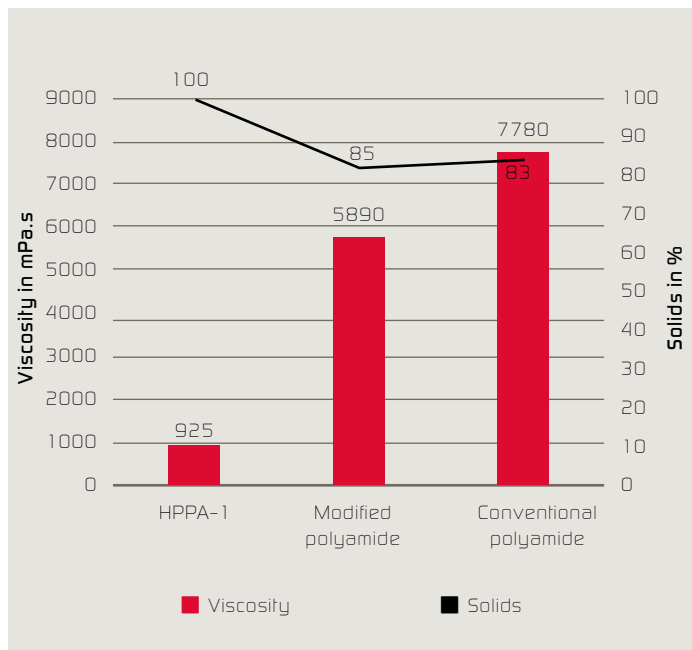


Figure 3: Epoxy resin clear-coats – Enhanced surface wetting observed with HPPA-1 compared with polyamidoamine.

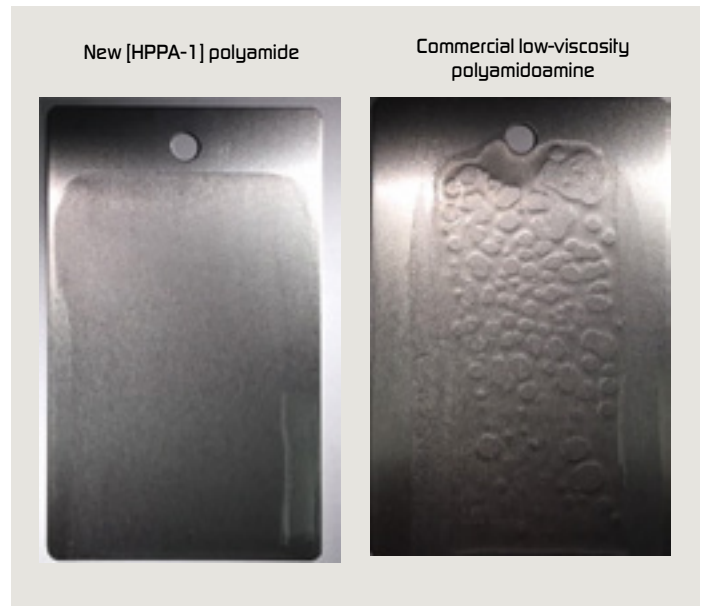
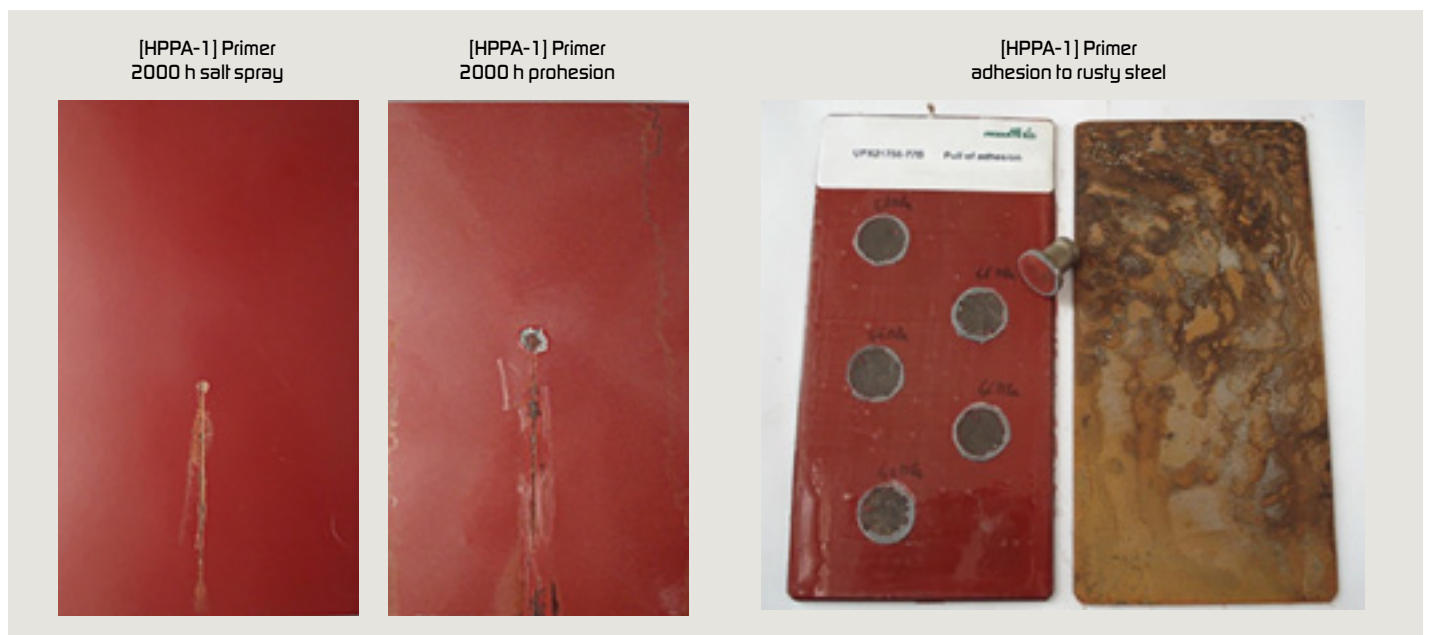


Figure 4: Anti-corrosive primer system based on HPPA-1 after accelerated weathering.



The requirement for lower VOCs and a fully cured crosslinked matrix in the case of high-solids systems is addressed by typically formulating the curing agents and epoxy resins with additional plasticisers, such as benzyl alcohol or alkyl phenols. These modifiers are also essential for improving system compatibility, drying rate, and adhesion. One potential drawback is that, in certain conditions, they may leach out while the coating is in service. This can affect its mechanical properties and lead to reduced flexibility and the development of internal stress. Consequently, the potential for a coating to deteriorate in performance increases over time. Furthermore, following recent changes in VOC definitions, the coatings sector considers benzyl alcohol to be a VOC [5], and so it can be difficult to reach the ultra-low VOC targets demanded by various coating sectors.

DEVELOPMENT NOVEL ULTRA LOW VISCOSITY POLYAMIDE CURING AGENT

Using lower-molecular curing agents and liquid epoxy resins yields a higher crosslink density in the cured film. This can confer improved benefits, such as improved protection against chemicals and corrosion, although reduced flexibility and increased coating brittleness may also result. Evonik has addressed these challenges by developing a proprietary n-alkylated polyamide polymer [6] which supersedes conventional polyethyleneamines. Similar to polyethyleneamines this proprietary technology

Table 3: Starting-point formulation for anti-corrosive primer ACP-01 using HPPA-1.

A-Component			Weight in g
Standard bis-A LER	Epoxy resin	Various	31.4
Epodil 742 diluent	Reactive diluent	Evonik	3.6
ZetaSperse 2100 agent	Dispersing agent	Evonik	1.0
BYK 57	Defoamer	Byk	1.0
Bayferrox 130M	Pigment	Bayer	5.0
Plastorit 000	Filler	Kremer	15.0
Sachtleben Micro	Filler	Sachtleben	26.0
Heucophos ZCP-plus	Anti-corrosive pigment	Heubach	6.7
10 ES Wollastocoat	Filler	Nyco Minerals	10.0
Bentone SD-2	Rheology modifier	Elementis	0.3
Xylene/butanol (4:1)	Solvent	Various	6.8
Total A:			106.8
B-Component			
Polyamide [HPPA-1]	Curing agent	Evonik	28.2

Primer [ACP-01] Properties

VOC	g/l	85
PVC	%	23
Vol. solids	%	91
Mixed viscosity	mPa s	1000
Mixed ratio	A:B (vol)	2:1
Pot-life, 23 °C	h	2
Thin-film set time, 23 °C	h	13



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can be employed to manufacture polyamides. The new polyamide (HPPA-1) curing agent [7] has an extremely low viscosity and contains no plasticisers or solvents. The handling properties of HPPA-1 and how this translates into providing coating systems of ultra-low viscosity at 100 % active solids are shown in Figures 1 and 2. Conventional low-viscosity polyamides based on C18 mono and C36 dimer acids derived from triethylenetetramine (TETA) are readily available, but many exhibit poor compatibility with LERs and need an induction time (1 h) prior to application. They dry slowly and invariably give rise to tacky, poor-quality films that are often unsuitable for application at temperatures < 10 °C. The new polyamide curing agent has a low initial viscosity and exhibits excellent compatibility with LERs, produces a good surface appearance and requires no induction time.

Figure 3 compares clear-coats based on the new polyamide with a commercial low-viscosity polyamidoamine for films applied at 23 °C without solvent or plasticiser.

Table 1: General properties of conventional solvent-borne and high-solids epoxy coatings.

Typical Properties	Solvent-Borne Epoxy Coating	Low-VOC Epoxy Coating
Epoxy resin	SER (EEW 500)	LER (EEW 190)
Drying time (walk on)	Fast	Slow
Pot-life	Long (6 h)	Short (1 h)
Barrier property	Excellent	Excellent
Chemical resistance based on weight increase	Moderate	Excellent
Flexibility	Excellent	Moderate
Solids by volume	Low	High
Curing agent	Polyamides	Cycloaliphatic adducts Mannich base
Solvent/plasticiser	Xylene, n-butanol	Benzyl alcohol

EEW = Epoxy equivalent weight

Table 2: General benefits and limitations of different types of curing agent.

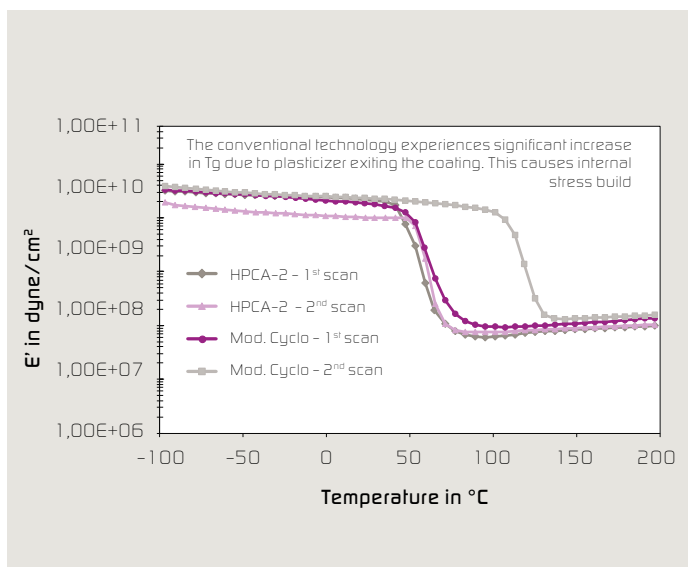
Curing agent type	Benefits	Limitations
Polyamides	High flexibility Long pot-life	High viscosity Slow through-cure
Aliphatic adducts	Fast drying	High viscosity EH&S profile
Cycloaliphatic adducts	Low viscosity Chemical resistance based on weight increase	Require plasticisers to fully cure
Amidoamines	Low viscosity	Poor low-temperature cure
Phenalkamines	Low-temperature cure	Poor overcoatability
Mannich bases	Rapid through-cure	EH&S profile (free phenols)

ANTI-CORROSIVE PRIMER FORMULATION AND PERFORMANCE PROPERTIES

The effectiveness of the new polyamide was demonstrated by formulating the curing agent into an anti-corrosive primer (Table 3). The formulation is a red iron oxide primer based on a modified zinc calcium polyphosphate having a VOC of 85 g/l and a 2-h pot-life. The primer can be spray-applied onto steel panels with conventional spray equipment immediately after mixing and without the need to add extra solvents. The drying time of 13 h at ambient is comparable to that of many solvent-borne polyamides.

Primer formulation (ACP-01) was spray-applied to grit-blasted (Sa 2,5) steel panels in double coats to yield a total dry film thickness of ± 200 µm. The panels were cured at ambient temperature for 10 days prior to accelerated corrosion testing. They were then scribed and assessed for field blisters as per ASTM B117. Scribe creep was rated as per ASTM D1654. At 1000-h intervals, one set of duplicate panels was removed

Figure 5: DMA storage modulus vs temperature of epoxy clear-coats.



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from the test cabinet and examined for blistering and rusting. The scribe areas were then scraped to expose the metal substrate and enable accurate scribe-creep measurements. The primer system was also found to provide enhanced adhesion to poorly prepared substrates. In this example, blasted steel panels were prepared by immersion in water for 4 weeks until significant rust build-up occurred. The panels were coated with (ACP-01) and pull-off adhesion was determined. The adhesion was compared with that of a modified polyamide and was found to provide comparable performance. The results for both accelerated weathering tests and adhesion to rusted steel are shown in *Table 4* and *Figure 4*.

DEVELOPMENT OF SOLVENT FREE CYCLOALIPHATIC CURING AGENTS

Further examples of curing agents based on our proprietary N-alkylpolyamine are two high-performance cycloaliphatic amine curing agents, HPCA-1 and HPCA-2. These curing agents [8] have been designed to deliver properties and performance that are typically attributed to hardeners based on aliphatic-cycloaliphatic amine adducts. Both are free of benzyl alcohol and (alkyl) phenol and exhibit ultra-low viscosity, thus facilitating the formulation of zero-VOC coatings. The unique structure of the base polyamine also allows greater control over the reactivity of the system. HPCA-1 has been designed to provide a long pot-life (3 h) and HPCA-2 has been formulated to yield coating systems that feature improved blush and carbamation resistance at low application temperatures ($\leq 10^\circ\text{C}$), thereby outperforming incumbent competitive cycloaliphatic amine systems [9]. The basic handling and performance properties, including gel time, curing rate and hardness development of clear-coats based on HPCA-1 and HPCA-2 are compared with those of an industry-standard, modified cycloaliphatic amine curing agent in *Table 5*. Both high-performance products have been formulated to provide 50 phr loading with a standard LER.

VERY GOOD BARRIER PROTECTION

A clear advantage of HPCA-1 and HPCA-2 over an industry-standard, modified cycloaliphatic is the low application viscosity achieved at 0 VOC – the standard cycloaliphatic has a VOC of 160 g/l due to the contribution of the benzyl alcohol in the curing agent.

The general performance properties of the clear-coats show that the new technology imbues coatings with good drying rate and very good through-cure, as measured by DSC at 23°C cure. Coatings also show good carbamation resistance, with improvements observed in the case of HPCA-2 cured at lower application temperatures. Electrochemical impedance spectroscopy (EIS) was used to measure the barrier properties of the clear-coats. In all cases, pore resistance (R_p) $> 10^8 \Omega$ was obtained after 24-h exposure to an aqueous salt solution. These figures show that the coatings provide excellent barrier protection and should deliver good all-round corrosion-resistance properties.

Primer formulations based on HPCA-1 and HPCA-2 are presented in *Table 6* and the general performance properties are summarised in *Table 7*.

VERY GOOD ADHESION AND SALT-SPRAY RESISTANCE

The general performance properties of the anti-corrosive primers based on HPCA-1 and HPCA-2 are very good. Both curing agents yield fast dry-to-touch and hard dry in the thumb twist test, corresponding to 15 h and 8 h for HPCA-1 and HPCA-2 respectively, with HPCA-2 being comparable to the standard modified cycloaliphatic amine used in this study. Due to the lack of benzyl alcohol in the HPCA technologies, the coatings exhibit superior Persoz hardness development, while maintaining good flexibility. All coatings provided very good adhesion to blasted steel (SA 2,5) and showed very good resistance to salt spray and Cleveland humidity.

Figure 6 shows the storage modulus as a function of temperature for clear-coats based on HPCA-2 and a conventional, modified cycloaliphatic amine benchmark.

SOLVENT FREE TECHNOLOGY MAINTAINS CONSISTENT IN-SERVICE TG DEVELOPMENT

Dynamic mechanical analysis (DMA) data of free films was obtained with the aid of a TA Instruments RSA II controlled strain rheometer in a tension rectangular geometry. Initial scans were obtained on 125 μm coatings following 14 days' curing at ambient. For the second scans, the coatings were cured for 14 days at 23°C , followed by an additional 2 h at 150°C in a circulating-air oven. Data was collected in isothermal 6°C steps from 100–200 $^\circ\text{C}$ at an applied oscillation fre-



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quency of 6.3 rad/s (1 Hz). The midpoint glass transition temperature (T_g) was measured as the peak in the tan delta curve. The T_g of the conventional cycloaliphatic amine demonstrates a significant increase (approx. 60 °C) between the initial and second scans. At the same time, the initial effective molecular weight between crosslinks, M_c , of 1020 g/mol drops to 930 g/mol. Such behaviour illustrates a potential deficiency of conventional epoxy thermoset systems. Non-reactive plasticisers are released from the coating during service, with the consequent danger of stress accumulation. HPCA-2 based coating shows no such deficiency. The changes in T_g between scans are within the error margins for a similar decrease in M_c .

COMPLIANCE WITH STRICTER REGULATIONS

Stringent emissions regulations and a growing need for more robust technologies that offer improved performance under adverse curing and service conditions are continuously driving new developments in the marine and protective coating sectors. As the final properties and performance of the coatings are mainly determined

by the binder system, the correct choice of resin and curing agent is essential if the specific application requirements are to be met. In epoxy coatings, a well-designed curing agent will address the difficulties described above and yield systems that offer a very good balance of pot-life, drying rate, viscosity, and flexibility. The new amine technology described here can be formulated into any type of 100 %-solids curing agents, and the formulations will exhibit low viscosity. Formulators can thus develop systems which are compliant with the newer, stricter emissions regulations. Furthermore, as this technology requires very little to no plasticiser to fully cure at ambient temperatures, the coatings are more likely to maintain their properties and performance throughout their service life. The very good compatibility with different epoxy resins reduces the tendency to blush and leads to a good surface appearance, eliminates induction time and allows the use of multi-component spray equipment. Additional benchmarking against conventional technologies reveals comparable corrosion resistance and a good pot-life combined with fast drying times and properties development, even at low temperatures.

Table 4: Performance data of HPPA-1 primer and a modified polyamide.

Polyamide	2000 h Salt spray		2000 h Prohesion		Adhesion to rusty steel	
	Field	Scribed	Field	Scribed	Strength psi	Mode of failure
Polyamide [HPPA-1]	10	9	10	8	899	Rust layer
Modified polyamide*	10	9	10	8	928	Rust layer

Salt spray - ASTM B-117; Prohesion - ASTM G-85; DFT ~200 µm; Rating: ASTM D714, ASTM 1654

Note: *Modified polyamide anti-corrosive primer formulation required a VOC level of 320 g/l to achieve comparable application viscosity.

Table 5: Performance properties of HPCA curing agents and a modified cycloaliphatic amine.

Property		HPCA-1	HPCA-2	Mod. cycloamine
AHEW	g/eqv	95	95	95
Viscosity, 23 °C	mPa s	150-250	300-600	300-600
Mixed viscosity, 23 °C	mPa s	780	850	750-900
Gel time, 150 g mix, 23 °C	min	150	35	40
TFST, pH III, 23 °C	h	13	7	8
TFST, pH III, 10 °C	h	24	14	20
Persoz hardness, 23 °C (7 d)		300	360	315
Persoz hardness, 10 °C (7 d)		200	375	125
Degree of cure via DSC at 23 °C (7 d)	%	>98	>98	>98
Carbamation resistance, 23 °C/10 °C		5/3	5/5	5/3
EIS (Rp)	Ω 1 h Ω 24 h	1.3 x 10 ¹⁰ 2.3 x 10 ⁸	9.6 x 10 ¹¹ 2.3 x 10 ¹⁰	3.4 x 10 ⁹ 9.3 x 10 ⁸
Cross-hatch adhesion, 23 °C (14 d)		5	5	5
VOC	g/l	0	0	160

a. Evaluated with bisphenol A/F resin; diluted with C12-C14-glycidyl ether, EEW=190

b. ASTM D3359; applied to S-36Q panels at 150 µm

Table 6: Starting-point formulation for anti-corrosive primer [ACP-02].

A-Component		Parts	B-Component	
Epoxy resin	EEW 190	31.4	Curing agent	17.5
Epodil 742	Reactive diluents	3.6		
ZetaSperser 2100	Dispersing agent	1.0		
Byk 057	Defoamer	1.0		
Bayferrox 130M	Pigment	5.0		
Plastorit 000	Filler	15.0		
Sachtleben Micro	Filler	26.0		
Heucophos ZCP-plus	Anti-corrosive pigment	6.7		
10 ES Wollastocoat	Filler	10.0		
Bentone SD-2	Rheology modifier	0.3		
Xylene/butanol 4:1	Solvent	1.5		

Notes:

1. Xylene/butanol added to achieve application viscosity of ~ 1000 mPa s
2. Curing agent, HPCA-1, HPCA-2 and modified cycloaliphatic
3. Total PVC = 30 %
4. HPCA technology: VOC = 60 g/l, vol. solids = 91.5 %
5. Mod. cycloaliphatic: VOC = 160 g/l; vol. solids = 81 %

Table 7: Performance properties of anti-corrosive primers based on ACP-02.

Property		Unit	HPCA-1	HPCA-2	Mod. Cyclo
Pensoz hardness	7 d	s	274	289	161
Impact test (direct)	7 d	kg cm	45	40	65
Gloss	60°	-	103	103	102
Thin-film set time (BK recorder)	pH III	h	9.5	6.5	7.5
Thumb twist	DTT	h	5.5	4.0	4.0
	DH	h	15.0	8.0	9.0
Cross-hatch adhesion	7 d	D3359	5B	5B	5B
Salt spray	1500 h		10	10	10
			No damage		
Cleveland humidity	1000 h		10	10	10

DTT = dry to touch; DH = dry hard;

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“Wide application window“

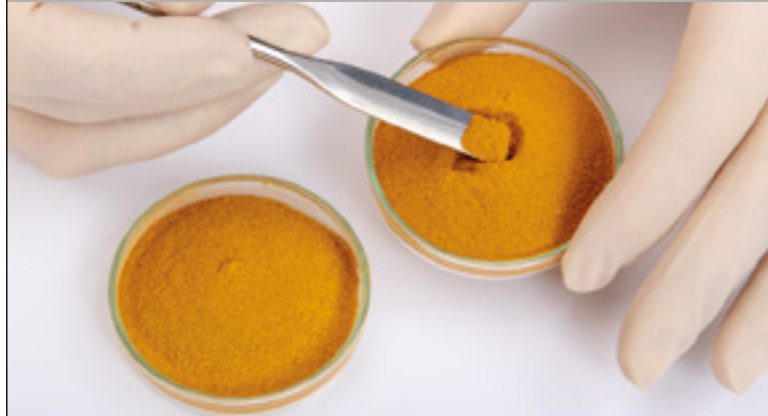
3 questions to Michael Cook

Where do you see the application window for the new curing agent? *This new technology is ideally suited for high performance corrosion resistant coatings, where high solids or solvent free formulations are required. With the growing requirement for solvent control the number of different applications are increasing. The curing profile allows for a wide application window at ambient and sub-ambient conditions, down to 10-15°C, for marine or general protective coating applications.*

What further development potential do you see in this new technology? *The chemistry which enables the formulation of VOC compliant systems can be further developed to allow for solvent free systems that will provide leading performance in 2K epoxy coatings for metal. The drive for low temperature can also be met with enhancements of this chemistry allowing for faster return to service and improved appearance after low temperature application.*

How much influence does the epoxy resin have on the final properties together with the new curing agent? *It is very important to have the right choice of resin and other components within a coating formulation to optimise the performance for a given application. This technology has been developed to provide formulation latitude and compatibility with a wide range of resins but to have optimal performance and application viscosity with no requirement for solvents or specialised equipment, low viscosity liquid epoxy resins would be recommended.*

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