

Innovative Polyamide Technology Delivering Long Overcoat Window

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Abstract

Growth in the global coating's market and economies coupled with ongoing VOC requirements continue to bring challenges in high performance protective coatings. Conventional high solid polyamide technology for two pack epoxies, provides outstanding performance and has become the industry standard for application in this sector. However, a major limitation to date is their limited re-coat window after applying the initial coating; this window or the time within which a second coating can be applied to result in good adhesion, has become of mounting importance. Increased geographical separation of the coating and fabrication processes has resulted in a requirement for protective primers with 3 to 6 months re-coat window. Conventional high solids epoxies have only a limited re-coatability, leading to higher cost for surface pre-treatment and extended down times, prior to application of subsequent coats. The innovative polyamide technology presented here offers significantly increased performance to negate this issue, delivering higher performance value to both the formulator and end applicator.

Introduction

The world is becoming a small place, so we are told, but in a time where continued economics are driving prices and margins down the distance and period between when a metal primer is applied to when it may be re-coated and fabricated is increasing. The coating of steel sections in the protective and marine coating sectors is becoming more and more geographically remote from where these are brought together into fabricated structures for bridges, ships and other structures. This global growth in the coating's market and coupled with ongoing VOC requirements continue to bring challenges in high performance protective coatings to the formulator and applicators alike.

The use of conventional high solid polyamide technology for two pack epoxy primers and tie coats provides outstanding performance, such as high adhesion to base substrate, good barrier properties and high anti-corrosive performance, and has become the industry standard for application in these sectors for applications such as universal primers. However, a major limitation to date is their limited re-coat window after applying the initial coating; this window or the time within which a second coating can be applied to result in good adhesion, has become of mounting importance. The increased geographical separation has resulted in a requirement for metal primers offering 3 to 6 months re-coat window with common overcoat polymer chemistries such as epoxy and polyurethane systems.

Conventional high solids epoxies have only limited re-coat window, leading to higher cost for surface pre-treatment and extended down times through water and chemical washing and in some cases mechanical abrasion. Sacrificial coatings are also employed, which by their name and nature are applied at site following primer application with sole purpose to offer a level of protection in transportation of metal components. This coating infers a further cost to the end user(s) in terms of both an additional coating step and the need then at fabrication site for its removal prior to re-coating. The objective of the paper presented here is to address these shortfalls of current technologies. New solutions are targeted and presented to the market place that offer end user(s) the possibility to reduce cost for pre-treatment and down times during the coating application process.

VOC requirements driving performance

Historically, prior to there being more stringent limits for volatile organic content (VOC), coatings offering good overcoatability were readily available. Typically these two-pack epoxy coatings were based on “solid” bisphenol A diglycidyl ether, epoxy resin (SER) and cured in combination with high molecular weight polyamide hardeners. The terminology “solid epoxy resin” is commonly used throughout the epoxy industry and refers to the physical state of the epoxy resin at room temperature. The most commonly used SER types are derived from bisphenol-A and have a number average molecular weight, $\overline{M}_n = 1050$, with $n \approx 2.5$. The high molecular weight of both binder components results in a cured coating with a relatively low crosslinkable, thermoset matrix. The low crosslinked density leads to coatings which are inherently flexible and as such offer a moderate degree of re-coatability. However, the coating systems due to their high solvent demand, cannot comply with the increasing needs within the coating sector for lower VOC limits and can therefore only be used in areas where these limits are not applicable or where stringent/expensive emission recycling is utilised.

With the introduction of maximum VOC limits in coating applications, development work in epoxy coatings has moved away from using SER to using so called “liquid” epoxy resin (LER). Analogous to SER terminology, a standard LER is in a liquid state at room temperature with an approx. viscosity of 12,000 mPa.s and characterised by $\overline{M}_n = 380$ ($n \approx 0.15$). The use of LER facilitates in achieving higher coating solids, however, this approach changes the handling and performance characteristics of the formulated coating. Reaction kinetic studies ¹ demonstrated that there can be a negative impact on the workable pot-life and the ability of the coating to dry (lacquer dry) when moving from SER to LER. In addition, the cured coating of a high solids epoxy system using LER results in a doubling of the crosslink density when compared with a conventional system based on SER. This change in crosslink density provides a coating with a lower degree of flexibility and potentially increased brittleness which has been found to limit the time period for extended re-coat. Typically without any surface treatment of the coating, systems need to be re-coated within a 1-10 day period. Beyond this period, any subsequent coating layer may be subject to delamination and intercoat adhesion failure.

Innovative polyamide technology

With Air Products’ knowledge of the protective and marine coating markets and our capability to develop new innovative technology through our global research and development groups, we have produced a new generation of polyamide curing agents. One such product is a modified polyamide solution of medium viscosity, which is designed for use with liquid epoxy resin in two-pack ambient cure coatings. The new polyamide concept offers significantly increased performance to overcome the aforementioned overcoating issues, whilst maintaining other properties such as cure speed and anti-corrosive performance that are prerequisites in the metal protection markets. In this paper, the new product will be referred to as LOPA-1, which stands for “long overcoat polyamide”.

The incumbent polyamide technology utilised in these sectors is represented by the two polyamide products, PA-2 and PA-3. Polyamide PA-2 is a low viscosity polyamide condensate, based on a TETA, C₃₆-dimer and C₁₈ fatty acids. Polyamide PA-2 has a high imidazoline content, which provides a route for low curing agent viscosity (10,000-15,000 mPa.s). Products of this type can readily be used with a LER to provide high solid coating formulations, where the VOC level is in the region of 290-350g/l. Polyamide PA-3 is an

adducted polyamide, offering improved compatibility and dry speed vs PA-2, while maintaining lower VOC demand. Formulations based on PA-3 can provide high solid coatings with VOCs as low as 250 g/l. The PA-3 type is now an established product in the marine & protective coatings market, due to the combination of a relatively low VOC and good overall performance properties, such as anti-corrosion, impact resistance and good flexibility.

Table 1 illustrates the comparative properties of the new polyamide LOPA-1 *versus* conventional polyamides, PA-2 and PA-3. The properties are for clear coats obtained with an unmodified liquid epoxy resin. As shown, the flexibility, direct impact resistance and dry speed of LOPA-1 are comparable to PA-3 and superior to PA-2. LOPA-1 also exhibits good reverse impact resistance compared to conventional polyamides. Finally, LOPA-1 has a low level of free, un-reacted amine, which reduces curing agent corrosivity and improves surface appearance by reducing the tendency of the coating to blush.

Re-coat window study

Contrary to existing two-pack high solid epoxy coatings based on LER, LOPA-1 offers the additional property of delivering coatings with an enhanced re-coat window. This means that coatings can be overcoated with a second coating based on either an epoxy or polyurethane formulation with good retention of the inter-coat adhesion. The re-coat window of LOPA-1 based clear coats with LER has been evaluated and compared with that of conventional polyamide PA-3. For optimum properties both polyamides were formulated at 70% of the theoretical stoichiometry with standard

Table 1. Comparative properties of selected polyamide products and clear coats

	Unit	LOPA-1 ^a	PA-2 ^b	PA-3 ^c
Neat Property				
Appearance		← Amber Liquid →		
Colour	Gardner	8	10	12
Specific Gravity, 25 °C		0.98	0.97	1.02
Amine Value	mg KOH/g	130	380	220
Viscosity, 25 °C	mPa.s	1,740	12,000	3,500
Solids	wt%	80	100	100
Equivalent Weight/{H}		250	95	150
Clear Coat Property²				
PHR ^{1,2}		90	50	70
BK Drying Time, 25 °C				
- phase 2	h	5	10	6
- phase 3	h	12	20	12
Persoz Pendulum Hardness, 25 °C, day7	s	100	120	100
Impact Resistance				
- Direct	cm.kg	100	40	84
- Reverse	cm.kg	40	10	20
Mandrel Bend	pass/fail	pass	pass	pass

a) Ancamide® 2652; b) Ancamide® 350A; c) Ancamide® 2050

1) part per hundred resin (PHR)

2) with liquid epoxy resin, EEW 182-192, $\eta = 12,000$ mPa.s

LER, which equates to 90 PHR and 70 PHR respectively for LOPA-1 and PA-3. After mixing the resin and curing agent, the resultant mixtures were diluted down to 75 wt% solids with a 1:1 w/w solvent mixture of xylene and n-butanol. Coatings were applied onto grit blasted steel (SA 2.5) at a wet film thickness of 200 μ m. After allowing each coating to achieve a

tack free state (4-8hrs), panels were then placed on an external (roof top) sun weathering panel for a period from 1 day to 84 days.

After each panel had been exposed to the set time period, the panels were overcoated with either the original epoxy formulation or a polyurethane clear coat, at a wet film thickness of 200 μ. The second coating was allowed to cure at 25 °C for 7 days, after which it was immersed in water at 25 °C for a further 7 days. Following this immersion period, panels were wiped dry with a tissue and subjected to the cross hatch cutter test. The cross hatch was then assessed for using the following ratings for the per cent damage found: 0% → 10; 20% → 8; 40% → 6; ... ; 100% → rating 0. A summary of the test method is shown in Figure 1.

Figure 2 shows the results of re-coat window. This is represented by the retention of adhesion over time following aging of the coating by sunlight exposure. For this, the adhesion retention was converted into a rating between 0 (no damage) to 10 (complete removal of the coating) and plotted *versus* exposure time. The formulation based on LOPA-1 demonstrates excellent re-coat window with very good adhesion retention after 84 days natural sunlight exposure. By comparison, the formulation based on PA-3 has good initial overcoatability, however, after 7 days exposure, the system shows severe signs of delamination when overcoated with the same epoxy

Figure 1. Test protocol for determination of re-coat window

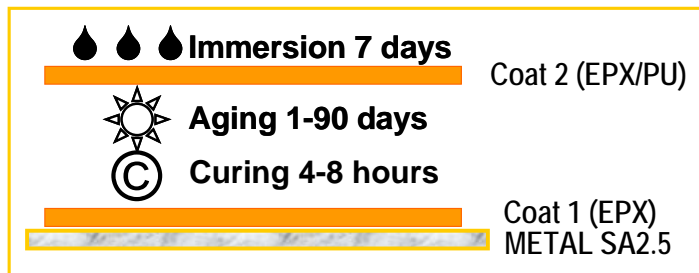
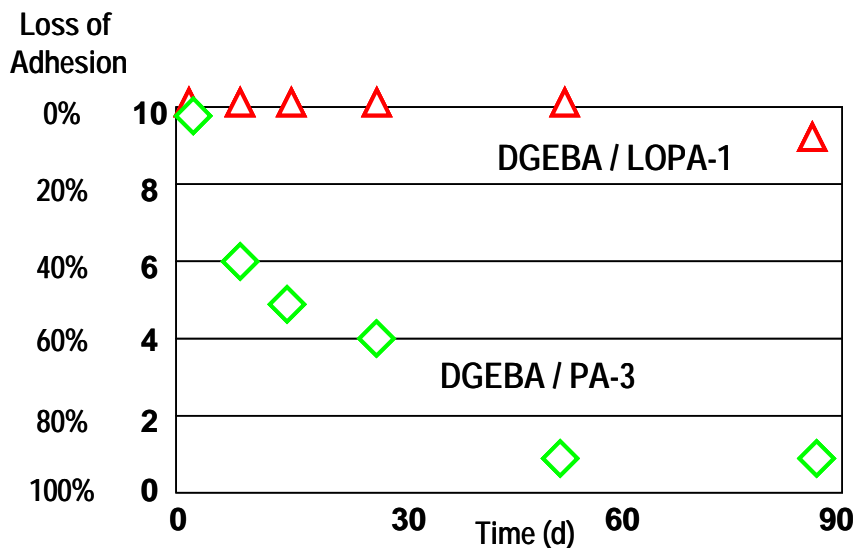


Figure 2. Test results of re-coat window study



based system. Figure 3 shows the cross hatch adhesion results of coatings based on LOPA-1 and PA-3 after 86 days exposure of the first coat to natural sunlight prior to applying the second coat. The tests conducted clearly show the superior overcoatability performance properties of LOPA-1 *versus* conventional polyamide technology. Additional

work using pigmented primers based on LOPA-1, included overcoating studies with epoxy and two-pack polyurethanes. Both systems provided similar excellent overcoatability, exceeding 3 months exposure².

Anti-corrosive primer formulation

Appendix 1 contains a starting point formulation based on LOPA-1 for an anti-corrosive primer. The typical properties of this formulation are presented in Table 2. The formulation is a red iron oxide primer based on a modified zinc calcium polyphosphate and offers 70 % volume solids at an acceptable VOC of 268 g/l. Further, the primer formulation has a low mix viscosity of approx. 550 mPa.s, with a pot life of 2 hours. The primer can be spray applied with conventional spray equipment following 10-15 minutes of mixing or brush applied to a steel substrate without the addition of extra solvents. Set to touch is reached after 4 hours while a dry to handle time is obtained within 15 hours.

Accelerated weathering resistance

The anti-corrosive primer formulation based on LOPA-1 was applied to grit blasted (SA 2.5), hot-rolled steel substrate panels. Using conventional spray equipment in double coats, a 120-150 micron dry film thickness resulted. Panels were left to cure at ambient temperature for 10 days prior to testing in salt spray, prohesion or continuous humidity at 45 °C following the respective standards listed in Table 3. Panels were scribed and evaluated for field blisters using US Federal Standard Test Method # 141A, Method 6461. Evaluation of scribe creep was rated in accordance with ASTM D1654. Coated panels exposed to humidity were also scribed and assessed for scribe creep and filed blistering. In addition, attention was paid to changes in visual appearance of the primer upon accelerated weathering.

Figure 3. Cross hatch adhesion after 84 days of aging by exposure to natural sunlight. Left picture shows coating based on LOPA-1; right coating based on PA-3

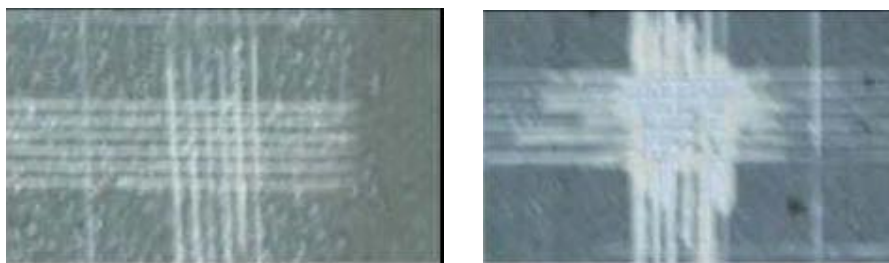


Table 2. Typical properties of anti-corrosive primer based on LOPA-1

Density Comp. A (g/ml)	1.75	Non-volatile (Vol% [Wt%])	70 [82]
Density Comp. B (g/ml)	1.07	Mix Viscosity, 25 °C (mPa.s)	550
Density Mix (g/ml)	1.57	Pot-life (h)	2
Mix ratio by volume	3:1	Set-to-Touch, ASTM1640 (h)	4
PVC (%)	35.8	Dry-Hard, ASTM1640 (h)	7
VOC (g/l)	268	Dry-to-Handle, ASTM1640 (h)	15

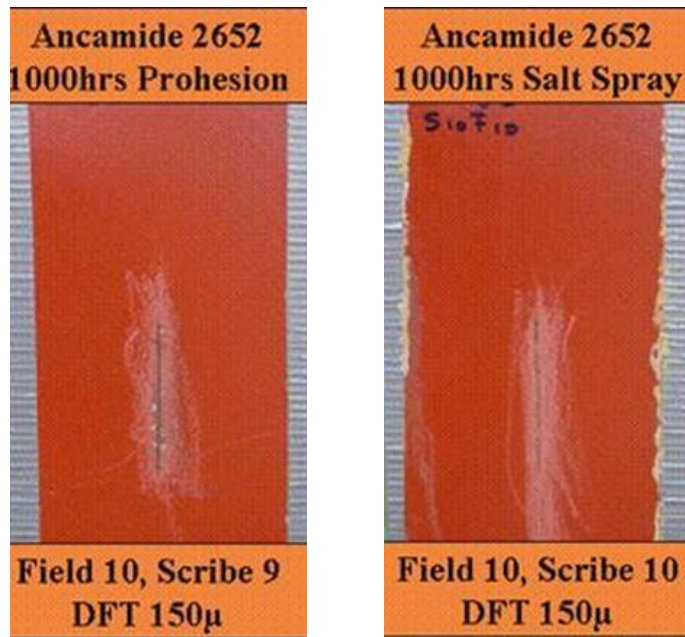
Table 3. Accelerated weathering resistance of primer based on LOPA-1 (150 μ DFT)

		Scribe Creep ¹	Field Blistering ¹
	ASTM ► ▼	D1654	US Fed.Std.# 141A Method 6461
5% Salt Spray (35 °C)	B117	9	10
Prohesion	G85-94	9	10

Continuous Humidity (45 °C)	D2247	10	10
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1) Scribe rating 0-10: 0 = worst, 10 = best; for blister size rating 0-10: 10 = no blisters observed

Figure 4. Primer based on LOPA-1 after 1000 hours prohesion (left) and salt spray (right)



Conclusions

Indeed, the world is becoming a smaller place due to globalisation of the coating's market. Intermediate structural metal components for construction now travel greater distances between the various stages of structure fabrication. Coatings with longer re-coat windows are required to allow for this and eliminate shortfalls of current technologies. At the same time, ongoing legislation require coating systems with lower VOC demand, which prevents use of conventional systems based on solid epoxy resin.

Conventional two-pack high solid epoxies based on liquid epoxy resin, though providing outstanding performance, have limited re-coat window after applying the initial coating. The new polyamide technology, LOPA-1, highlighted within this paper, when formulated with liquid epoxy resin, demonstrates a significant performance improvement of the re-coat window compared to existing 2K epoxy technology. Using a test protocol where the initial coating is aged by natural sunlight, re-coat windows of LOPA-1 exceeded three months when overcoated with a two-pack epoxy or polyurethane. In addition, an anti-corrosive primer formulation based on LOPA-1 with liquid epoxy resin was presented. The formulation demonstrated excellent corrosion resistance as determined by the accelerated weathering test data. The combination of long overcoatability, while retaining flexibility and corrosion protection, make LOPA-1 a preferred choice in a growing and increasingly demanding protective coatings market.

References

¹ Walker, F.H.; Dubowik, D.A.; Starnier, W.E., International Waterborne, High Solids and Powder Symposium, New Orleans, February 1999

² Internal results, Air Products and Chemicals, Inc.

Appendices

Appendix 1. Anti-corrosion primer formulation based on LOPA-1

				Anti-Corrosive Primer
A-Component				Parts by Weight
1	Liquid Epoxy Resin	D.E.R.™ 331	Dow Resins	217.0
2	Dispersant	Nuosperse® 657	Elementis Specialties	5.0
3	Thixotrope	Bentone SD®-2	Elementis Specialties	8.0
4	Solvent	Xylene		145.0
5	Solvent	n-Butanol		20.0
6	Pigment	Bayferrox® 130M	Lanxess	80.0
7	Pigment	Heucophos® ZCPP	Heubach International	125.0
8	Filler	Blanc Fixe Micro®	Sachtleben Chemie	180.0
9	Filler	Wollastocoat® 10ES	Nyco Minerals	120.0
10	Filler	Mica White 325M		100.0
				1000.0
A-Component Manufacture Procedure				
<ul style="list-style-type: none"> ● Charge components 1-3 and mix at low shear ● Slowly add solvent, pigment and fillers while increasing speed to 10-20 m/s ● Grind with high speed disperser at approx. 10-20 m/s for 20 minutes ● Complete grinding to achieve Hegmann gauge 7 				
B-Component				
11	Curing Agent	Ancamide® 2652	Air Products and Chemicals, Inc	205.0
Total				1205.0