

Novel TETA-Free Polyamides for 2K Epoxy Systems

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The first commercial polyamides from C18 dimerized fatty acid with primary amines took place in the late 40's. Since then, this class of polyamides has been widely used in 2K epoxy coatings and adhesives. Formulations based on these polyamides provide excellent adhesion, flexibility and corrosion resistance, and thus have found wide market acceptance in the marine and protective coating market sectors to provide protection to bridges, offshore platforms, and merchant shipping both new builds and repair.

Market dynamics for higher ethylene amines have resulted in significant price increases and potential tightness of supply of a key base amine, Triethylenetetramine (TETA), used in polyamide manufacture. In response to the raw material dynamics, an alternative, commercially viable amine stream has been identified. This new amine stream has a similar structure to that of TETA and as been evaluated as an alternative technology within the synthesis of base polyamides.

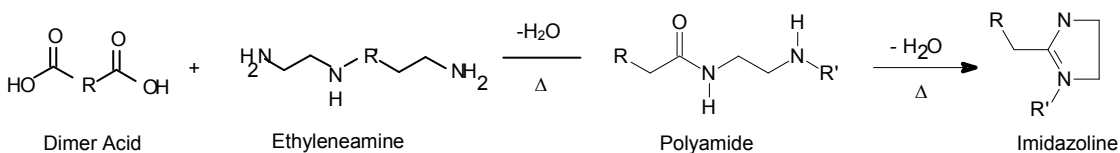
This paper describes performance properties of a new class of polyamide those are either TETA-free or have reduced TETA demand, and that are designed to be performance offsets in existing commercial epoxy formulations. This innovative technology will allow the continuity of supply of polyamides at a competitive cost, with minimum reformulation work, and will augment existing business based on current high growth and continued demand in the coatings and adhesives' sectors.

Introduction

Polyamide curing agent for 2K epoxy systems are obtained by reacting C18 dimerized fatty acid, Tall Oil Fatty Acid (TOFA) with ethylene amines as the reaction between dimer acid and amine takes place, water is removed to form the amide link, the reaction can then continue under higher process temperatures to form the cyclic imidazoline. By varying the ratio of imidazoline/amide the general handling and performance properties of the resultant polyamide can then be controlled (figure 1) and the most common are: Triethylenetetramine (TETA) and Tetraethylenepentamine (TEPA).

Formulations containing typical polyamides provide excellent adhesion, flexibility and corrosion resistance at reasonable low cost and thus have found wide market acceptance in the marine and protective coating market sectors to provide protection to bridges, offshore platforms, and merchant shipping both new builds and repair.

Figure 1
A reaction of ethylene amines and Dimer Acid



TETA is a core raw material to produce polyamide for 2K epoxy systems and it is used also in the synthesis of polyamide adducts, waterborne curing agents and other formulated products. Ethylene Amines supply dynamics suggest a general tightening in the market due to production changes coupled with market growth. Thus, TETA (and the other homologs) have seen unprecedented cost increases over the last 2-3 years. A realistic scenario is to expect TETA price to continue to rise, and tightness of supply to continue with direct impact on the current supply situation and market pricing for polyamides.

A new class of polyamides, which are TETA free, or have reduced TETA demand, was developed by Air Products and Chemicals Inc. This innovative technology, will allow the continuity of supply of polyamides at a competitive cost, with minimum reformulation work needed to replace the conventional polyamides by the new technology.

Amine development

The first stage was to identify an amine capable to replace TETA in polyamides and other classes of curing agents for 2K epoxy systems. The amine should have properties as close as possible to TETA, while having reduced exposure to the ethylene amine market dynamics, and thus a more stable cost structure and more stable price.

Table 1 compares the properties of TETA and the amine selected to use as its replacement.

Table 1
Properties comparison between TETA and the new amine

	New Amine	TETA
Amine Value (mg KOH/g)	1202	1404
Color (Gardner)	<2	<2
AHEW	29	28
Formulation (phr)	15.3	14.6
Gel Time (100g mix @ 25°C)	30	32
Peak exothermic temp (°C)	225	238
Tg (°C)	106	119
Vapor pressure (mmHg, 25°C)	0.7	2.1

PA1: High viscosity solvent based polyamide

PA1 is the first product developed in a series of TETA-free or reduced TETA demand polyamides products. This specific curing agent is TETA-free and it is targeted to replace its analogue containing TETA and as a result can be used at the same polyamide loading level.

PA1 is a low viscosity, solvent based polyamide; supplied at 70% solids in xylene. It is intended for use with solvent based solid epoxy resins in the development of high performance, corrosion resistant coatings for the protection of steel and concrete. When used with type 1 solid, Bisphenol A epoxy resins (e.g., Dow DER 671X75 or Epon 1001 X75), PA1 offers fast lacquer dry, rapid mechanical property development, good adhesion to the steel substrate and excellent long-term humidity and corrosion resistance.

Solvent based coatings can be formulated using this product which can then be used for a wide variety of industrial maintenance and marine applications.

Clear coating formulation based on PA1

The model formulation in the Table 2 was used to determine the properties of a clear coating formulation using PA1 and a commercially available polyamide based on TETA. After mixing the resin (component A) and curing agent (component B), a 15 to 30 minutes induction time is recommended prior to application, to ensure excellent compatibility between the two components.

Table 2
Clear Coating Model Formulation

		Clear Coat
A-Component (g)		
1. Epoxy Resin	Type 1 Bisphenol A epoxy (EEW= 450-550), 75%	410.00
2. Solvent	MIBK	80.00
3. Solvent	Dowanol PM	10.00
		500.00
B-Component (g)		
1. Curing Agent	PA1 Air Products	155.00
2. Solvent	Xylene	140.00
3. Solvent	Dowanol PM	140.00
		435.00
Total A+B		935.00

In the clear coat formulation with solid epoxy resin, PA1 exhibits a high degree of flexibility, good direct impact resistance and excellent reverse impact resistance. As shown in Table 3 all these properties are comparable to commercially available polyamide based on TETA.

Table 3
Clear Coat Performance Properties

Property	PA1	Commercial Polyamide
Direct Impact (cm.Kg)	200	200
Reverse Impact (cm.Kg)	200	200
Dry Speed BK Phase II [hrs]	4:30	6:00
Dry Speed (+2.5% K54)	2:00	2:30
Specular Gloss 60°	142	140
Pendulum Hardness		
Day 1	80	70
Day 3	205	200
Day 14	300	300
Cylindrical Mandrel Bend (mm pass)	3	3
Cross Hatch Adhesion (dry)*	Gt0	Gt0

*Cross hatch adhesion Gt0 = no loss of adhesion

Anti-corrosive primer formulation based on PA1

Formulation PA-X70P1 (Table 4) is a low volume solids (43%), medium PVC (34%) primer, with a 3:1 mix ratio by volume, based on epoxy resin to amine hardener. The initial viscosity of the formulated resin base is 2,300 mPa.s and the mix viscosity of the system is 500 mPa.s with a total VOC of 485g/l. The primer formulation is compatible with a variety of different let down solvents (including xylene, n-Butanol, MIBK, methoxy-propanol, etc) and can be further let down if required for additional spray applications. The coating formulation can be applied with conventional spray equipment or brush applied to the steel substrate. After application the primer is dry to handle after 5 hrs.

Formulation PA-X70P1 has been evaluated for corrosion resistance properties using salt spray, humidity and prohesion resistance accelerated weather tests. After 1000 hrs exposure, coatings exhibit excellent corrosion resistance. No signs of field blisters have been detected using the above weather tests, with panels exhibiting no scribe creep in the salt spray test and some minor damage around the scribe when subjected to the prohesion test study. For comparative purposes, a commercially available polyamide based on TETA was also included in the test study as the "industry" standard reference. In all the corrosion resistance tests carried out, both PA1 and the commercial product demonstrated comparable performance.

Performance evaluation of primer system

Both primers were evaluated in 5% salt spray, and in continuous humidity at 35°C. They were also evaluated using a prohesion - cyclic weathering tester, and Cleveland - constant humidity exposure, following a 10 day ambient cure of applied coatings.

Coatings were applied to grit blasted, hot rolled steel (SA2.5), using conventional spray equipment, in double coats to give coatings with a 75-100µ dry thin thickness (DFT). In salt spray, (ASTM B-117) panels were scribed and evaluated for field blisters using the US Federal

Standard Test Method 141a, Method 6461 and the scribe creep was rated in accordance with ASTM D-1654. Similar evaluations were made for panels placed in the prohesion cabinet (ASTM G85-94). Panels exposed to humidity were not scribed and coatings were assessed for blistering only. These tests also included evaluations for changes in visual appearance.

Table 4
Anti-corrosive primer formulation

			Anti-Corrosive Primer
A-Component (g)			
1. Epoxy Resin	Type 1 Bisphenol A epoxy (EEW= 450-550), 75%		280.00
2. Solvent	MIBK		80.00
3. Solvent	Xylene		110.00
4. Solvent	n-Butanol		30.00
5. Filler	Blanc fix micro		100.00
6. Filler	Talc 10MO		100.00
7. Filler	Heucophos ZPO	Heubach	140.00
8. Filler	Bayferrox 130M	Bayer	150.00
			1000.00
A-Component Manufacture Procedure:			
<ul style="list-style-type: none"> • Charge components 1-3 and stir homogeneous at low shear • Slowly add components 5-8 and then mix under high shear for 15-30 mins until Hegman gauge 7 is achieved 			
B-Component (g)			
1. Curing Agent	PA1	Air Products	106.00
2. Solvent	Xylene		59.00
3. Solvent	Dowanol PM		35.00
			200.00
Total			1200.00

After mixing Part A and B, apply a 15-30 minute induction time prior to application.

Corrosion Resistance

Anti-corrosion resistant primers based on PA1 and the commercially available polyamide based on TETA, were evaluated for salt spray and constant humidity resistance. The results obtained are presented in Table 5-7 and Figures 1 and 2. Following 1000hrs salt fog exposure, formulations containing both polyamides curing agent exhibit excellent resistance. Both formulations also demonstrated excellent humidity resistance with no signs of field blistering being observed following 2000 hrs continuous testing.

Table 5
Salt Spray Resistance [1000hrs]

Formulation	Scribe Creep	Field Blistering	Blister Size
PA1	10	10	10
TETA based polyamide	9	10	10

5% salt spray, cabinet temperature 35°C - ASTM B-117, film thickness 75-100µ
Rating: 10 = Best (no blisters), 0 = Worst

Figure 1
Salt Spray Resistance [1000hrs]

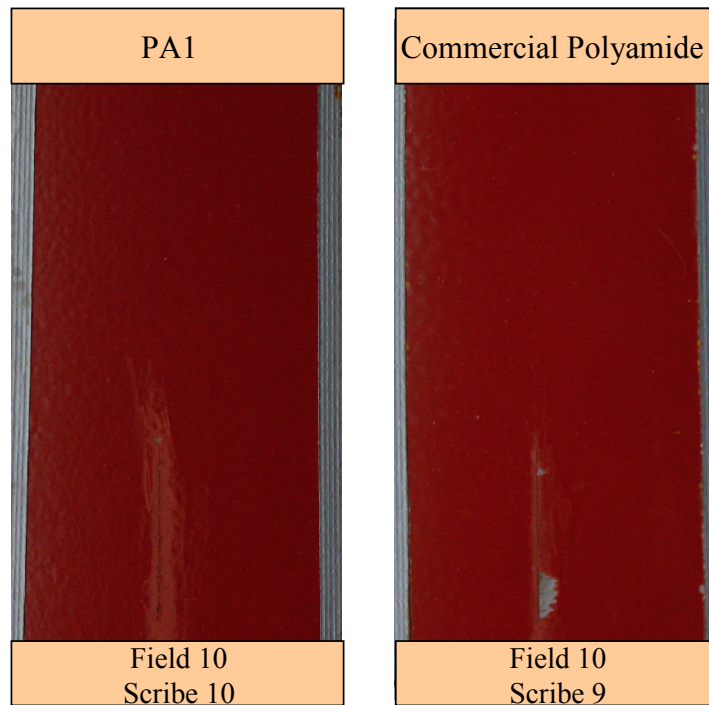


Table 6
Prohesion Exposure [1000hrs]

Formulation	Scribe Creep	Field Blistering	Blister Size
PA1	7	10	10
TETA based polyamide	6	10	10

Prohesion ASTM G85-94
Film thickness 75-100µ. Rating: 10 = Best, 0 = Worst
For blister size, rating 10 = no blisters observed

Figure 2
Prohesion Exposure [1000hrs]

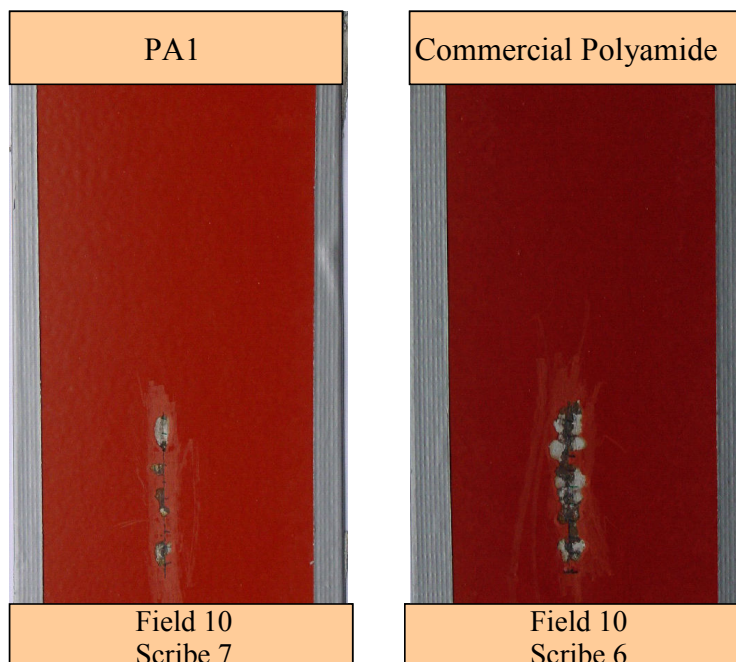


Table 7
Cleveland Humidity Exposure [2000hrs]

Formulation	Field Blistering	Blister Size
PA1	10	10
TETA based polyamide	10	10

Continuous 100% humidity exposure - ASTM D-2247, cabinet temperature 50°C
 Film thickness 75-100µ. Rating: 10 = Best, 0 = Worst
 For blister size, rating 10 = no blisters observed

PA2: Solvent-free medium viscosity polyamide

PA2 is medium viscosity polyamide, supplied at 100% solids. The product is intended for use in combination with or without other amines in 2K epoxy systems. When used with a standard Diglycidil Ether of Bisphenol A (DGEBA) type liquid epoxy resin (EEW=190) PA2 offers excellent handling, corrosion resistance, physical properties and adhesion to various substrates.

Film Properties

In a clear coat formulation PA2 also exhibits a good degree of flexibility. As shown in Table 8, the direct impact resistance of PA2 is comparable to a conventional commercially available polyamide based on TETA. PA2 and the commercial product have the same amine value. PA2 formulations can also be accelerated using tertiary amine accelerator. Levels can be varied to achieve the desired dry speed properties, with the preferred level in the 2.5-5.0% range based on PA2 use level.

Table 8
Clear Coat Performance Properties

Property	Polyamide PB ^(*)	Commercial Polyamide ^(*)
Direct Impact (cm.Kg)	40	40
Reverse Impact (cm.Kg)	10	10
Dry Speed BK Phase II [hrs]	9:30	10:00
Dry Speed (+2.5% K54)	5:00	5:30
Specular Gloss 60°	90	95
Cross Hatch Adhesion (dry)	5B	5B

(*) Tested with liquid Bis A Diglycidil ether (EEW 190),
Cross hatch adhesion 5B = no loss of adhesion.

Starting Point Formulations

Formulation PB-1 (Table 9), with solid epoxy resin, is 62% volume solids. PVC is 37% for formulations with PA2 and the commercially available polyamide based on TETA. The primer formulation is compatible with a variety of different let down solvents (including xylene, n-Butanol, MIBK, methoxy-propanol, etc) and can be further let down if required for additional spray applications. The coating formulation can be applied with conventional spray equipment or brush applied to the steel substrate.

Formulation PB-1 was evaluated for corrosion resistance properties using salt spray, Distilled Water Immersion and NaCl 3.5% immersion at room temperature. After 1000 hrs exposure, coatings exhibit excellent corrosion resistance. No signs of field blisters have been detected using the above tests, with panels exhibiting no scribe creep in the salt spray test.

Performance Evaluation

Formulation PB-1 was evaluated in 5% salt spray, distilled water immersion at room temperature and NaCl 3.5% immersion at room temperature, following a 10 day ambient cure of applied coatings.

Coatings were applied to grit blasted, hot rolled steel (SA2.5), using conventional spray equipment, in double coats to give coatings with a 75-100 μ dry thin thickness (DFT). In salt spray, (ASTM B-117) panels were scribed and evaluated for field blisters using the US Federal Standard Test Method 141a, Method 6461 and the scribe creep was rated in accordance with ASTM D-1654. Similar evaluations were made for panels placed in NaCl 3.5% immersion at room temperature and Distilled water immersion. Panels exposed to distilled water immersion were not scribed and coatings were assessed for blistering only. These tests also included evaluations for changes in visual appearance.

Table 9
Formulation PB-1: Anti- Corrosive Primer Formulation

A-Component (g)			Anti-Corrosive Primer
1. Epoxy Resin	Type 1 Bisphenol A epoxy (EEW= 450-550), 75%		210.50
2. Epodil L	Epodil L	Air Products	23.00
3. Epodil 748	Epodil 748	Air Products	21.00
4. Anti-Terra U80	Anti-Terra U-80	Byk Chemie	3.10
5. Additive	Bentone SD-2		11.50
6. Solvent	MIBK		19.10
7. Solvent	Xylene		61.20
8. Solvent	Dowanol PM	Dow	15.30
9. Filler	Barite		153.10
10. Filler	Talc 400 mesh		191.40
11. Filler	Quartz 400 mesh		191.40
12. Pigment	Zinc Phosphate	Heubach	30.50
13. Pigment	Bayferrox 130M	Bayer	68.90
B-Component (g)			
1. Curing Agent	PA2	Air Products	109.27
2. Additive	Ancamine K54	Air Products	7.36
3. Solvent	Xylene		119.97
4. Solvent	Butanol		60.00
Total A+B			1296.60

After mixing Part A and B, apply a 30 minute induction time prior to application.

Corrosion Resistance

Anti-corrosive primers based on PA2 and the industry standard based on TETA was evaluated for salt spray, distilled water immersion at room temperature and NaCl 3.5% immersion at room temperature. The results obtained are presented in Table 10, 11 and 12. After 1000hrs salt fog exposure, both formulations exhibit excellent resistance and also demonstrated excellent water and salt water resistance with no signs of field blistering being observed following 1,000 hrs continuous testing.

Table 10
Salt Spray Resistance [1000hrs]

	PA2	Commercial Polyamide
Overall rating	9 – 10	9 – 10
Scribe creep	0 – 1 mm	0 – 1 mm
X-hatch adhesion after 1,000 hours	5B	5B

5% salt spray, cabinet temperature 35°C - ASTM B-117, film thickness 75-100µ
Rating: 10 = Best (no blisters), 0 = Worst

Table 11
Distilled Water Immersion @ RT [1000hrs]

	PA2		Commercial Polyamide	
	Before immersion	After 1,000 hours	Before immersion	After 1,000 hours
X-Hatch Adhesion	5B	5B	5B	5B
Gloss/Appearance	No change	No change	No change	No change

Table 12
NaCl 3.5% Immersion @ RT [1000hrs]

	PA2		Commercial Polyamide	
	Before immersion	After 1,000 hours	Before immersion	After 1,000 hours
X-Hatch Adhesion	5B	5B	5B	5B
Gloss/Appearance	No change	No change	No change	No change
Scribe creep	0 mm	0 mm	0 mm	0 mm

Summary

The results obtained offer conclusive evidence that there is a practical alternative to TETA congenital polyamides in the 2K coatings and adhesives sectors. The requirement for a viable alternative, based on this innovative amine technology, allows the formulator the ability not only to maintain business at a time where market dynamics will lead to product shortages and escalating costs, but provides the foundation for continued growth and competitive advantage through the period of supply and demand imbalance. These developments to commodity polyamides further provide increased price stability and can in part effectively 'shield' some of the price volatility expected over the projected shortfall in the market.

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