

Thin-film MMB epoxy applied to pipe interior
Courtesy of the ICI Devco Coatings

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E OLD CLIMATES AND short production schedules are challenges for coating pipe and tank internals. If it is not sub-freezing temperatures or high humidity to contend with, it is the financial and production urgency of retrofitting the pipe or tank with a chemical- or abrasion-resistant lining and quickly returning it to service. Delays may cost a company significant revenues each day that a tank is out of commission. Compounding the issues are questions of solvent emissions from coatings, regulatory compliance, and ease of application of the coating.

So how are the issues addressed? One approach is to use solvented, thin-film modified aliphatic amine Mannich base (MMB) epoxies that cure down to 0 F (-18 C). Another approach is to use solvent-free, ultra-high thick-film, advanced hybrid cycloaliphatic (AHC) epoxies, some of which cure down to 32 F (0 C). Both types have rapid cure features that yield high cross-link density, and both perform well in ag-

gressive immersion service in the petrochemical, water and wastewater, pulp and paper, and railcar industries. AHC epoxies are used in single-coat applications.

With proper equipment, rapid-cure MMB and AHC epoxies can also make ideal field- and shop-applied coatings. They can also help address the paramount issues of tank leakage and secondary containment, where the costs of remediation and cleanup are potentially devastating.

It all sounds too good to be true. In fact, it can be too good to be true, and it is easy to see why. Without well-written specifications, judicious coating selection, independent third-party inspection, and qualified applicators using suitable application equipment, coating calamities can occur. There are no miracle coatings. Coating success or failure for pipe and tank internals and externals usually boils down to 3 major and overlapping components: the chemistry, testing, and application/inspection of the coating. All things being equal, when these 3 necessary requirements are met,

good performance can be obtained, and coating life can be maximized.

This article will examine the key parameters of chemistry, testing, and application of the rapid-cure MMB and AHC epoxy linings applied to either steel or concrete surfaces.

Lining Selection: The Influence of Chemistry

The genesis of epoxy technology hails back to 1942, when epoxy resins were first discovered. Since then, diglycidyl ethers of Bisphenol-A (DGEBA) and Bisphenol-F (DGEBF), which contain 2 reactive epoxy groups, have been the most frequently utilized backbones of epoxy resins (Fig. 1). Available in low molecular weights from 340 (n=0, where n is the number of repeat-

- modified aliphatic amine,
- polyamine adduct, and
- amido amine.

How exactly do epoxy coatings work? A simple analogy should prove helpful. In the same way the integrity of a steel tank depends on the strength, size, composition, and connection of its steel components—not to mention its careful design by an engineer and assembly by competent iron workers—so the chemical, mechanical, and thermal properties of two-component epoxies depend on the type and strength of the chemical bonds, the spatial configuration of the final three-dimensional network of atoms and molecules, and the expertise of the products formulation chemists and applicators.

On a theoretical level, epoxy coatings are barriers that impede water transport through the film and so provide corrosion mitigation by halting or retarding the cath-

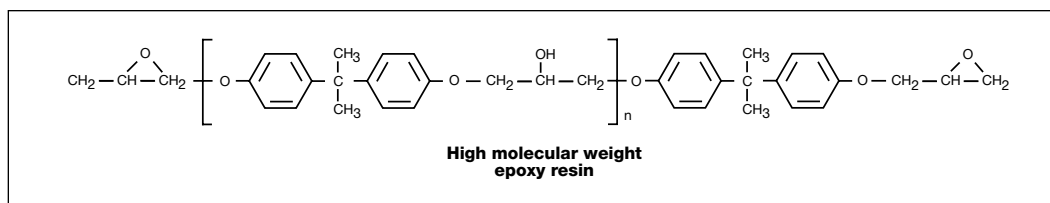


Fig. 1 - Epoxy resin
Figures courtesy
of the authors

weights of 8,000 (n=26), the basic low molecular weight epoxy resin (n=1) is a low viscosity, honey-like liquid in contrast to higher molecular weight epoxy resins (n=2 to 26), which are high viscosity or solid, and may require blending with solvents.

Performance can vary dramatically within the generic classification of two-component epoxies, largely because of the many converters to cross-link epoxy resins (Table 1). A sampling of cross-linkers includes

- polyamide,
- cycloaliphatic amine,
- aromatic amine,
- aliphatic amine,

ode reaction in a corrosion cell. Practically, however, an epoxy coating is permeable to oxygen and water and does not necessarily control corrosion through barrier protection because the level of water uptake is more than sufficient to cause corrosion.¹ Epoxy films are also permselective, having electrical charges that allow or prevent the transport of ions through them. So in reality, they provide protection by interposing a high electrical resistance into the corrosion cell circuit, acting as a filter to ions and a barrier to current flow between anodic and cathodic sites.

In the late 1940s, two-component epoxies were invented², and for the past 50 years or so, these condensation polymers

**Table 1
General Comparison of Epoxy Curing Agent Types**

Low Temperature Cure		Chemical Resistance	
	Water	Acids	Solvents
Excellent	Excellent	Excellent	Very Good
MMB*	MMB	Aromatic amine	Aliphatic amine-A**
AHC***	AHC	AHC	AHC
Aliphatic amine-MB****	Polyamide	MMB	Cycloaliphatic amine-MB
Aromatic amine	—	Cycloaliphatic amine-MB	MMB
Cycloaliphatic amine-MB	Amido amine	Cycloaliphatic amine-A	Cycloaliphatic amine-A
Cycloaliphatic amine-A	Cycloaliphatic amine-A	Aliphatic amine-A	Aromatic amine
Aliphatic amine-A	Cycloaliphatic amine-MB	Aliphatic amine-MB	—
Polyamide	Aliphatic amine	Amido amine	Polyamide
Amido amine	Aromatic amine	Polyamide	Amido amine
Poor	Very Good	Moderate	Poor

* MMB = Modified aliphatic amine-MB
 ** A = Adduct
 *** AHC = Advanced hybrid cycloaliphatic
 **** MB = Mannich base

have earned a reputation for good to excellent long-term durability, resistance to harsh chemical conditions, and resistance to corrosion. However, until the 1970s, one of the limitations of the matured two-component epoxy technology was an inability to achieve cure at temperatures below 40 F (4 C). To see why and how the problem has been overcome, it is necessary to examine the epoxy curing mechanism.

The Amine-Epoxy Cure Mechanism

It is instructive to explore what happens at the molecular level when an applicator mixes the epoxy base and an amine converter, first with traditional epoxy technology and then with the rapid-cure MMB and AHC epoxy coatings. The four-stage curing mechanism (A through D) and the chemical reactions (Fig. 2) have been much simplified.

The A Stage

In the A stage, the applicator combines the 2 components, and cross-linking has not begun. The material is homogeneously mixed and applied, and the molecules have a high degree of motion and low viscosity.

The B Stage

This is when all the shenanigans take place. In the B stage, one of the active hydrogens in the primary amines in the converter reacts with an epoxy group. This results in formation of a hydroxyl group (OH) and a secondary amine. The secondary amine then reacts with an epoxy group on another resin molecule to form a tertiary amine and yet another hydroxyl group. Normally, most of the primary amines react before the secondary amines react, and the solvents evaporate, first by convection and then by diffusion.

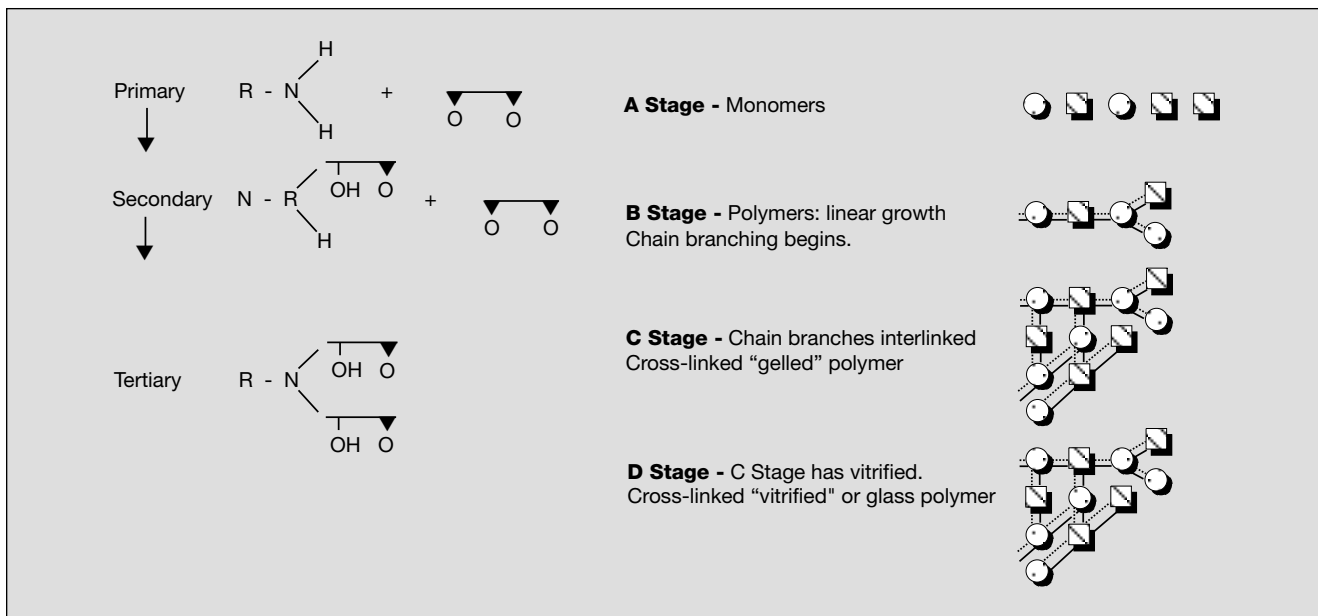


Fig. 2 - Amine epoxy reaction

In the B stage of a typical epoxy reaction, the viscosity increases, and the molecular mobility decreases, restricting movement of unreacted secondary amines. The reaction is very temperature sensitive. Linear growth and branching now take place to form a glassy, thermoplastic solid. As the molecular network grows and the viscosity increases, the secondary amines find it harder to move around and join with another epoxy molecule in what now amounts to a big molecular spaghetti-like network. If the temperature drops below 50 F (10 C), the viscosity increases still further and the reaction slows or stops altogether (around 40 F [4 C]). Some Mannich bases cure below 40 F (4 C), but the curing takes longer and depends on the converter.

As the chain length increases, individual chains or polymer segments begin to entangle, and so-called "network flow" occurs. Solvents or thinners trapped in the film may detract from satisfactory adhesion or resistance to water and chemicals. Depending upon the exposure and type of converter, should a temperature drop arrest the cross-linking in the B stage, raising the temperature again may or may not reinitiate the cure reaction. The epoxy is then said to have "B staged" and is only partially cured, brittle, and therefore compromised in terms of expected performance. Fortunately, not all epoxies are in this category.

The C and D Stages

The C, or gelled stage, progresses slowly. In it, the polymer chains have interlinked to form a giant and essentially complete polymer. The polymer becomes vitrified, or motionless (glass formation), and the molecules are in their final three-dimensional structure. Finally, post-curing will drive the reaction to complete cross-linking and the D stage. Below a critical temperature, called the glass transition temperature (T_g),³ the spaghetti-like polymer segments do not have sufficient energy to slide past one another. The glass transition temperature is a function of the degree of cross-linking, intra-chain stiffness, and intermolecular polar forces.

Throughout the cure, the generation of hydroxyl groups is most important because they largely provide adhesion to polar sites on surfaces such as steel or concrete. The tertiary amines formed in the C and D stages invariably act as catalysts and speed up the overall curing process.

MMB Epoxy Chemistry— Thin-Film Linings

Up until the late 1970s, the speed of the sequential curing reactions was rather slow, and typically only about 60 to 75 percent cure was achieved at room temperature, leaving unreacted secondary amines in the dried film and obtaining limited production

Table 2
Time-Temperature Curing Data for
Epoxy Coatings with Different Curing Agents.
Dry to Recoat Time in Hours (ASTM D 1640,
Fed Std. 141B Method 4061)*

Temperature	AHC** Epoxy (30 mils**** dft)	MMB*** Epoxy (6 mils dft)	Conventional Epoxy Polyamide (6 mils dft)
20 F (-7 C)	NR*****	24 hours	NR
40 F (4 C)	3.5 to 4 hours	10 hours	21 hours
60 F (16 C)	1.75 hours	4 hours	8 hours
80 F (27 C)	1 hour	2 hours	4.5 hours

* Conditions such as excessive film thickness, poor ventilation, and excessive humidity cause deviation.

** AHC = Advanced hybrid cycloaliphatic

*** MMB = Modified Mannich base

**** 1 mil = 25 micrometers

***** NR = Not recommended

of adhesive hydroxyl groups. Moreover, the low temperature limit on most amine converters was approximately 45 to 50 F (7 to 10 C), at which temperature the percentage of cure would be much lower. The way to get lower temperature curing was to add a third component called a “kicker” or accelerator. This addition compromised the system, rendering it more brittle and porous. Curing agents derived from Mannich bases—a reaction between amines, formaldehyde, and phenol—offered unique advantages with regard to low temperature cure and good chemical resistance. But the drawbacks of these epoxies were their lack of flexibility and short pot lives.

In 1979, rapid-cure modified aliphatic amine Mannich base-derived epoxies (MMB) emerged and overcame these drawbacks while giving even lower temperature cure. There were several notable differences in their converter formulations. First, the molecular structure of the converter was novel and a planar shape rather than a boat, chair, or zigzag shape. The design enabled cross-linking and curing to take place more readily. This improved the reaction kinetics, which involved catalysis and molecular mobility in the “big molecular

spaghetti.” Second, the spacing, number, and availability of active hydrogen atoms on the converters were configured to give more flexibility and a greater degree of curing.

In this way, manufacturers with MMB epoxy technology engineered coatings with the following advantages.

- The reactions of the secondary amines were accelerated.
- Steric or size hindrance of the secondary amines was reduced.
- Production of catalytic tertiary amines was increased.
- The concentration of hydroxyl groups was increased for greater wet and dry adhesion.
- Molecular mobility and superior wetting out of surfaces were obtained at low temperatures.

A long hydrocarbon chain in the converter contributes towards the flexibility of MMB epoxies. The hydrophobic polyaminic substituents in the benzene ring provide unique water resistance and high cross-link density. The phenolic group offers cure at low temperatures.

With epoxy coatings, anti-corrosive pigments and lamellar pigments, such as

Table 3
Time-Temperature Curing Data for
Epoxy Coatings with Different Curing Agents.
Dry-Through Time in Hours (ASTM D 1640,
Fed Std. 141B Method 4061)*

Temperature	AHC** Epoxy (30 mils**** dft)	MMB*** Epoxy (6 mils dft)	Conventional Epoxy Polyamide (6 mils dft)
20 F (-7 C)	NR*****	60 hours	NR
40 F (4 C)	24 hours	30 hours	48 hours
60 F (16 C)	12 hours	10 hours	23 hours
80 F (27 C)	8 hours	8 hours	11 hours

* Conditions such as excessive film thickness, poor ventilation, and excessive humidity cause deviation.

** AHC = Advanced hybrid cycloaliphatic

*** MMB = Modified Mannich base

**** 1 mil = 25 micrometers

***** NR = Not recommended

micaceous iron oxide and non-leaving aluminum, can sometimes assist in corrosion mitigation and increase the diffusion requirement for the ingress of oxygen, moisture, and ionogenic materials. However, these pigments offer limited advantages to MMB epoxies with their high level of cure, cross-link density, and adhesion.

The chemical nature also affects the application properties. In the typical two-coat, 10- to 12-mil (250- to 300-micrometer) dry film thickness MMB epoxy lining, the primer can be recoated in 2 to 3 hours at 80 F (27 C) or 24 hours at 20 F (-7 C). (See Tables 2 and 3.) The MMB epoxies have easily workable viscosities, long pot lives (at least 3 to 4 hours at 77 F [25 C]; 6 hours at 20 F [-7 C]), and easy mixing ratios (3:1, 4:1), collectively ideal for use with airless spray equipment.

Given their 65 to 80 percent solids by volume range, they may be applied by brush, roller, and conventional equipment. However, 2 disadvantages of MMB epoxy technology are their yellowish converters—which limit certain color availability and consistency for exterior use—and their difficult brush or roller application because of their rapid cure features.

AHC Epoxy Chemistry— Ultra-High Thick-Film Linings

Aromatic amines (where an amine is attached to a benzene ring) offer excellent chemical resistance when combined with epoxy phenolic resins. But they are very slow to react and normally need a catalyst or accelerator to speed up the reaction.

In contrast, cycloaliphatic amines have rings similar to the benzene rings except that they are fully saturated. These converters have much better molecular mobility and better speed of reaction compared to aromatic amines. The advanced cycloaliphatic hybrid (AHC) uses more than one converter to cross-link an epoxy phenolic novolac resin, yielding a balance between speed of reaction and cross-link density.

The rapid-cure AHC epoxy coatings are 100 percent solids and, depending upon service requirements, can be applied in one-coat applications between 25 and 125 mils (0.5 and 3 mm) dft without runs or sags. Steel or concrete pipes and tanks lined with the AHC epoxies can be returned to service in as little as 8 hours from the time of application (Tables 2 and 3). As with all coatings, the most important criteri-

on for curing is time-at-temperature.

The solvent-free and low-odor AHC epoxy is self-priming and can be spray applied in a single, ultra-high thick-film coat. Should an applicator add a small amount of solvent, the cure time of an AHC epoxy lining system will be extended, but the final cure properties will not be impaired.

These AHC systems were developed in the 1990s. The benchmark chosen for optimum chemical resistance of this epoxy technology was satisfactory long-term immersion in methanol and other aggressive, petroleum-based chemicals. Formulations with only single converters have limited effectiveness, whereas properly formulated multi-converter AHC epoxies can withstand constant immersion in methanol, as well as a whole range of solvents, fatty acids, and mineral acids such as glacial acetic, hydrochloric, and concentrated sulfuric acids. AHC epoxies contain specially selected anti-corrosive pigments.

Attaining complete cure at low temperatures can be achieved with liquid epoxy resins utilizing multifunctional diluents, 2 or more converters with high secondary amine content, and certain mobilizing agents. For highly aggressive immersion resistance, post-cure drives the reaction to completion, increases T_g , and increases film strength and chemical resistance.

Ease of application is required for desired performance. The AHC coatings are best applied using hot twin-feed plural component equipment, not particularly easy to use unless the contractor has the appropriate spray equipment and experience with this type of technology. The mixing ratios of these coatings are typically 2:1, and their pot lives at 77 F (25 C) are normally in the 6- to 45-minute range (Table 4). Viscosities are temperature dependent and very important for good application. For example, at 77 F (25 C), an AHC epoxy can have a viscosity like honey; at 100 F (38 C), a viscosity similar to skim milk; and

at 40 F (4 C), a viscosity like molasses. One AHC epoxy coating had viscosity values of 19,000, 29,000, and 100,000 cps at 100 F (38 C), 70 F (21 C), and 40 F (4 C), respectively. Spraying at the proper temperature is critical to trouble-free application.

Some experienced applicators can and do routinely and successfully apply AHC epoxies with high ratio standard airless spray equipment utilizing pre-heat and in-line heater viscosity control.

To Accelerate or Not To Accelerate?

That is the question. At the job site, the artificial heating system might fail, or a slow-curing epoxy might impede an applicator's progress, but the owner will still need the pipe or tank to be returned quickly to service. A decision may be made to add an accelerator. In the short term, this approach seems painless enough. But the consequences can be injurious to coating performance and the owner's expectations of long and maintenance-free coating life.

Why so? Although many acidic and basic accelerators exist, typical field-added accelerators are often based on tertiary amines such as DMP 30 (tris 2,4,6 dimethylaminomethyl phenol). These can be water sensitive and highly reactive in homopolymerizing the epoxy. They can also lead to a more brittle and permeable film with less water and chemical resistance. Reality often arrives with a thud if too much accelerator is used. The coating might crack and disbond or cause intercoat delamination even before it is placed in immersion service. A shortened pot life can also make application more difficult.

One way to avoid this scenario is to use a rapid-cure MMB epoxy. The reason lies in an internal accelerator or catalyst, which comprises part of the structure of the converter itself. This intrinsically accelerates the reaction between the amine and epoxy groups even at low temperatures (0 F [-18

Fig. 3 - Underside of a 140-foot (43-meter) floating roof tank lined with a 50- to 60-mil (1- to 1.5-millimeter) AHC epoxy for sour service
 Courtesy of Industrial Environmental Coatings Corp.

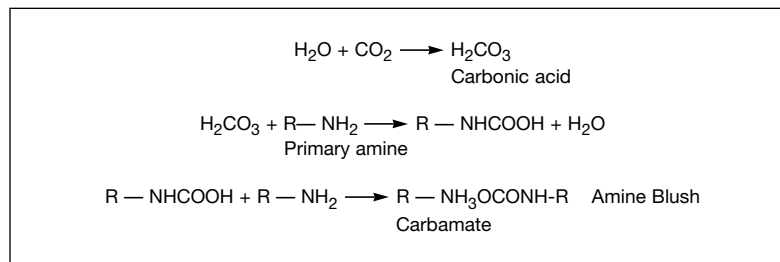


Fig. 4 - Amine blush—carbamate formation from amines in moist air

C) without the addition of an accelerator at the manufacturing or application stages. As shown in Fig. 2, the internally catalyzed MMB epoxy coatings produce the maximum number of adhesive hydroxyl groups.

Resistance to Amine Blush

During a multi-coat application process, the applicator should be aware that at high humidity and low temperature, an epoxy coating might “amine blush” or “sweat.” If not carefully removed by washing, or cleaning with a suggested 1:1 glycol ether/water mixture, this clear and water-soluble blush, or surface contaminant film, can lead to intercoat adhesion failure of a topcoat. This phenomenon is also similar to one occurring in solvented systems with poor ventilation, which can give an appearance of blushing. The latter is actually a case of “solvent washing,” where the solvent produces a sticky residue on the film.

An amine blush is the reaction product of the primary amine groups seen in Fig. 2 with atmospheric CO₂/H₂O to form substituted amine carbamates that dimerize and exude to the epoxy surface (Fig. 4).

Rapid-cure MMB epoxies have some key attributes that discourage the amine blush phenomenon. In the converter portion of the MMB epoxy, most of the available primary amines have been converted

into secondary amines during the manufacturing process. The secondary amines do not react with CO₂ and do not produce an amine blush. Residual primary amines have been taken up in an intra-molecular acid-base reaction, which renders them unavailable for carbamate formation. The molecular structure is very hydrophobic in the rapid-cure MMB epoxies because of the converter technology, discouraging uptake of both moisture and polar gases such as CO₂, lowering the concentration of gas in the film, and further reducing any tendency to amine blush. Blushing is minimized with AHC epoxies because of the fast cure speed and the preheating of the material to 90 to 105 F (35 to 40 C) before spraying. Even if blushing does occur with AHC epoxies, it is not a problem because of the single-coat application.

Tolerance for Wet and Damp Surfaces

The thorny issue of “wet” versus “damp” surfaces must be addressed. Unfortunately, to the authors’ knowledge, there is no universal definition of “wet” versus “damp” that would quantify the amount of water present in either description. With respect to dampness, the abilities of the MMB epoxy are summarized as follows.

- MMB epoxies are essentially neither moisture- nor temperature-sensitive.
- Common sense must prevail with respect to “wet” or “damp” surfaces. MMB epoxies should not be applied to surfaces on which beaded or free-standing water is present. This condition can be confirmed by wiping a clean hand (salt-free) on the surface and inspecting the hand to ensure no visible water is observed.
- All steel and concrete surfaces must be free of ice and frost.

MMB and AHC coatings are excellent surfactants, and MMB epoxies are particularly tolerant of damp surfaces, readily dispersing water molecules. Yet despite this quality, the authors strongly advocate hu-

Table 4
Comparison of Rapid-Cure AHC and MMB Epoxies

	AHC Advanced Hybrid Cycloaliphatic	MMB Modified Mannich Base	Conventional Epoxy—Polyamide
Volume solids	100 percent	80 percent	60 to 80 percent
Minimum cure temperature	32 F (0 C)	0 F (-18 C)	45 F (7 C)
Pot life at 77 F (25 C)	30 to 45 minutes	3 to 4 hours	4 to 8 hours
Recommended dry film thickness	30 mils*	10 to 12 mils	10 to 12 mils
Number of coats	1	2	2
Spray application	Plural component (preferred) Airless spray with in-line heaters	Airless spray	Airless spray
Time to immersion 77 F (25 C) 32 F (0 C)	8 hours 30 hours	18 hours (water) 40 hours (water)	7 days Not applicable
Cathodic disbondment (CAN/CSA-Z245.20-M92) (1.5V SCE, 80 C, 48 hrs, 3% NaCl)	5 mm** (avg) disbondment	Not available	Not available
Cathodic disbondment (Modified ASTM G 8) (5V SCE)	Not available	No blisters or failure after 3 years	Blisters after 8 months
EIS Log Z (ω - cm^2)	10.5	10.2	10 to 10.2
Autoclave (max temp resistance)	250 F (121 C) maximum	200 F (93 C) maximum	180 F (82 C) maximum
Adhesion to steel	1,800 to 2,100 psi***	1,500 to 1,800 psi	700 to 1,100 psi
Taber abrasion (ASTM D 4060) (CS-17, 1,000 g)	18 mg	109 mg	120 to 180 mg

* 1 mil = 25 micrometers

** 1 mm = 40 mils

*** 1,000 psi = 6.895 MPa

midity control for the application of these coatings for pipe and tank internals for immersion service applications. Dehumidification is often recommended.⁴

Lining Selection: The Influence of Laboratory and Field Testing

Before a recommendation is made for a pipe or tank lining, many factors should be assessed, such as field and laboratory resistance to chemical exposure; high temperature excursions; delamination from cathodic protection, erosion, cold wall effects, or os-

motric disbondment; thermal expansion of the coating versus steel; adequate flexibility to accommodate steel movements; and mode of failure in chemical exposure (cracking, blistering, and chemical attack).

In addition, coatings typically have an optimum film thickness where coating defects are minimized (e.g., pinholing, foam, solvent entrapment, uneven pigment distribution), and chemical/physical properties are maximized (e.g., flexibility, strength, cross-linking). The optimum total dft cannot be predicted but must be determined experimentally. Although many manufacturers perform tests to establish such data, it is often the case that owners want inde-

pendent third-party testing to comparatively evaluate the effects of chemical and physical stresses on candidate coating systems.

Criteria and test methods for screening or pre-qualifying organic coatings include the following.

- Applicator friendliness
- Cathodic disbondment (ASTM G 8, G 95, or CAN/CSA Z245.20-M92)
- Electrochemical impedance spectroscopy (EIS)
- Autoclave test (NACE TM 01-85-88)
- Standard Atlas Cell test (Modified NACE TM 01-74-91)
- Pressurized Atlas Cell test (Modified field NACE TM 01-74-91)
- Salt fog (ASTM B 117)
- Chemical cycle tests
- Adhesion pull-off strength (ASTM D 4541-89)
- Impact test (Modified ASTM G 14-88)

A cautionary note: No one coating will necessarily excel or pass all laboratory tests. Also, just because a coating does well in any particular test does not mean it will perform satisfactorily under real life conditions. The merit of the test results is that, taken together, they "indicate" field performance. But the data must not be overinterpreted. In addition, field testing of panels lined with candidate linings should be strongly considered. Suitably coated panels can be immersed in the chemical for several months, withdrawn, and evaluated in the laboratory.

Manufacturers have amassed considerable test results for a variety of epoxy linings including rapid-cure MMB and AHC epoxy coatings.

Some of the more commonly used tests for epoxy coatings are shown in Table 4 and described below.

Cathodic Disbondment (CD)

The AHC epoxy coating demonstrated a small amount of disbondment as shown in Table 4 (less than 8 mm; other 100 percent

solids epoxy coatings can give similar results). This result exceeds the CD pre-qualification in the CSA standard for fusion-bonded epoxy coatings.

Although the MMB epoxy was not examined in this particular test, in a modified ASTM G 8 cathodic disbondment test there was no deterioration or blistering even after 3 years at -5,000 mV.

Electrochemical Impedance Spectroscopy (EIS)

Coating impedances are measured at a frequency of 0.1 Hz. The key for interpretation of the impedance data⁵ is diagrammatically represented⁶ in Fig. 5.

Table 4 shows that the rapid-cure MMB and AHC epoxy coatings have very large electrochemical impedance values, especially AHC lining systems (log Z around 10.5). Impedance values of freshly applied high-performance epoxy linings are higher than those of field-retrieved panels of the same lining. Defect-free coatings with high impedance exhibit good corrosion control. When impedance is seen to diminish as a function of time, it indicates increased permeation and ion exchange rates within the coating film, i.e., precursors to coating degradation.

Autoclave Test

Two-coat applications of MMB epoxies perform well in the autoclave up to a maximum of 200 F (93 C), but not higher. Up to this temperature, MMB epoxies offer good performance and distinct application advantages for year-round applications. However, epoxy coatings with far superior temperature and pressure resistances are available, based on either multi-functional epoxy resins (e.g., epoxy phenolic novolacs) cured with aromatic amines or hybrid cycloaliphatic amines. Performance of AHC epoxies and thin-film epoxy phenolic novolacs is good to 275 F (135 C) and 1,000 psi in gaseous mixtures with up to 40

percent H₂S.

Standard and Pressurized Atlas Cell

AHC epoxies outperform MMB epoxies in Atlas Cell tests. In fact, AHC epoxies have

performance have been observed not only because of inadequate project organization of the contracting company, but also because of lack of experience and project management of the assigned crews, who

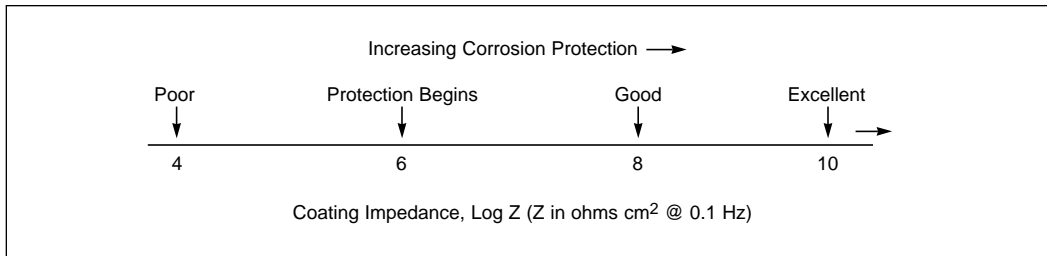


Fig. 5 - Corrosion protection of organic coatings⁶

been shown to markedly outperform many high-performance immersion-grade epoxies in these independent tests. In the authors' experience, however, with thousands of tanks lined with high-performance epoxies, the Atlas Cell test has limited merit in indicating field performance.

Adhesion

The MMB and AHC epoxies have excellent adhesion values of 1,000 to 2,000 psi (ASTM D 4541-89) on blast-cleaned steel. Higher values are obtained when the coatings are force cured.

Lining Selection: The Influence of Application

Selection Includes the Crew

Although not typically part of a pre-qualification and audit process, the authors recommend that the specification authority both qualify and audit not only the independent third-party inspection company and the preferred contractor, but also the specific personnel, crew, and application equipment for the project at hand. (This recommendation is based on the authors' field experience.) To some degree, this recommendation parallels the process of selecting a coating manufacturer. Project delays, escalating costs, and poor coating

may not be very familiar with procedures and equipment.

Surface Preparation Requirements

Long-term performance of newly lined or relined pipes and tanks relies upon close attention to detail of surface preparation and application.⁷ As with other coatings for permanent immersion in aggressive chemicals, MMB and AHC epoxy linings require surface preparation to SSPC-SP 10 (Near-White) or SSPC-SP 5 (White Metal) standards for optimum results. Key factors to consider are shown in Table 5.

Fabrication details, surface finish requirements, and proper design requirements for substrates to be coated for immersion service should be in accordance with NACE-RP 01-78-95.

Also before blasting begins, the applicator must assure that the surface is free of oil, grease, salt deposits, and other foreign material. If not removed, these surface contaminants would be driven into the profile of either steel or concrete and very likely would cause premature coating failure. Old pipes and tanks will be contaminated with chemicals and must be thoroughly cleaned before blast cleaning. Soluble salts and emulsifiable contaminants are often best removed using pressurized hot water and specialized detergents, particularly those with a sequestration agent that readily re-

Laboratory Testing

Cathodic Disbondment (CD)

Although it can preserve steel pipes or tanks, cathodic protection can often be detrimental to the performance of a coating. Coatings designed for use with cathodic protection must be capable of withstanding blister formation from electroendosmosis where water and ions are transported through the coating under an electrical potential. *[Editor's Note: For additional description, see this month's Trouble with Paint, pp. 17-34.]* In an active cathodic protection system, the cathodically generated hydroxyl ions necessitate excellent alkali resistance properties from the epoxy coating. In harsh environments, disbondment is initiated and propagates around a discontinuity or holiday in the coating. Cathodically generated hydroxide ions beneath

the coating produce a highly alkaline condition at the polymer/substrate interfacial region. At excess stress potentials of -5,000 mV, the pH at the epoxy/steel interface exceeds 14.

The test methods are ASTM G 8, ASTM G 95, or CAN/CSA Z245.20-M92. The latter method is similar to ASTM G 95, except the CSA method offers alternatives for test temperature and duration.

An initial holiday of 3.2 mm is made by drilling the coating applied to a blast-cleaned (SSPC-SP 5) panel. The experiment consists of making a seal between a cylinder and coated sample using silicone sealant centered on the initial holiday. The cylinder is filled with a 3 percent NaCl solution, and the samples are polarized cathodically by impressing a stress potential of -1,500 mV for 28 days.

Electrochemical Impedance Spectroscopy (EIS)

EIS measures the AC electrical resistance (impedance) of a coating at low frequency and is a good tool for evaluating organic coating performance.

The impedance of a coating is related to its permeability to water, gas, and other corrosives. Hence, the phases in an EIS test are often water, oil, and gaseous mixtures. The higher the impedance of a coating, the lower its permeability to corrosives, and hence the more protective the coating. Low impedance implies a high permeability and possibly underfilm corrosion.

EIS measurements were made with an EG&G PAR flat cell and the Gamry Instruments Inc. Electrochemical Impedance Spectroscopy mea-

moves soluble chlorides and sulfates. In the authors' experience, soluble chloride levels for high-performance, immersion-grade linings should be less than 10 $\mu\text{g}/\text{cm}^2$ and preferably less than 5 $\mu\text{g}/\text{cm}^2$.

Some of the most innovative manufacturers with specialized detergents have demonstrated the effectiveness of their materials in the Alberta Oil Patch, where thousands of tanks, vessels, and pipes are coated each year. In the case of heavily pitted steel, it is best to clean the surface first with the appropriate water/detergent cleaning procedure, dry blast, and be prepared to wash and blast again if necessary.

There are several opinions concerning abrasive blast profile requirements. Past experience has indicated to the authors that the shape of the profile is far more important than the height. The depth of the profile has less of a performance effect on adhesion than does the degree of roughness established. The preferred anchor pattern for MMB and AHC epoxies is the same as

other immersion service linings, i.e., a jagged tooth with a profile of 2.5 to 4.0 mils (63 to 100 micrometers). Abrasives must be sharp, angular, dry, and of good quality. When tested according to ASTM D 4940 (based on a 1:1 ratio of abrasive to deionized water), the conductivity should not exceed 150 microsiemens. The deionized water extract should have a chloride content of 25 ppm or less.

Before the lining system is applied, the blast-cleaned surface should be thoroughly vacuumed, with special attention given to pitted and horizontal areas. Sweeping or blowing down is not sufficient to remove residual abrasive media. If coatings are applied over residual media, coating adhesion and performance could be compromised. A simple test to confirm that the blasted substrate has been properly cleaned is to apply a strip of masking tape to the substrate, remove it, and visually inspect the underside of the tape for contaminants. Although subjective because the

surement system (Model CMS100 [potentiostat] and Model CMS300 [SoftFra]). The area of coating exposed for evaluation in the flat cell was 1.0 cm². A saturated calomel reference electrode (SCE) and platinum counter electrode were used.

The cell solution was 5 percent NaCl, unstirred at 74 F (23 C). The frequency was ramped from 5,000 Hz to 0.05 Hz, with 3 impedance measurements per decade. The AC amplitude was 50 mV (RMS), except for degraded coatings, for which it was 25 mV (RMS).

Autoclave Test

For over 20 years, the autoclave test has been used successfully to screen organic coatings. The test is used to compare the reactions of one or more coatings to conditions that simulate an anticipated service environment in tanks and vessels. Exposed to liquids, gases, temperature, and pressure, the coatings that demon-

strate the least reaction are considered to be the most reliable for use in that service.

Candidate coatings were applied to blast-cleaned steel (SSPC-SP 5) and exposed to the test environment for 96 hours. Typical test conditions are as follows:

- Temperature: 150 F/66 C and 180 F/82 C
- Pressure: 3.5 MPa/500 psi
- Water: Distilled
- Hydrocarbon: Kerosene/toluene @ 9:1 by volume
- Gas: 5 percent hydrogen sulfide, 5 percent carbon dioxide, 90 percent methane
- Duration: 96 hours

Standard and Pressurized Atlas Cell

These test cells are pressurized with gas mixtures (typically H₂S, CO₂, and CH₄ [methane]) to evaluate performance and any reaction when experiencing a simulated cold wall ef-

fect. This happens when the internal environment of a substrate is higher in temperature than the external, such as in uninsulated heated tanks. The cold wall effect increases the rate at which the coating is permeated by the environment. If there are sites of low adhesion at the coating/substrate interface, the environment will accumulate, causing blisters and decreased overall adhesion.

Typical test conditions are as follows:

- Water: Distilled
- Hydrocarbon: Kerosene/toluene @ 9:1 by volume
- Gas: Vapor
- Duration: 28 days
- Temperatures: Internal 110 F/43 C; External Ambient 90 F/36 C. ○

masking tape will never be completely clean, if there is a high degree of contaminant, the cleaning should continue until a predetermined, acceptable degree has been established.

After abrasive blasting is completed, but before coating application begins, a simple black light hydrocarbon detection test is recommended, as are chloride and pH tests.

Application

One of the most important aspects of a successful coating application is for the applicator to be able to competently transfer and apply the product. Whether using plural component, airless, or conventional application equipment, the viscosity of the product and its compatibility with the equipment are critical for success. The quality control manager should assess viscosity and compatibility.

Viscosity is the measurement of a fluid's resistance to flow at a given temper-

ature. It is very important to store coatings in controlled environments of 75 to 90 F (24 to 32 C) when they are to be applied under adverse conditions. Heating results in less energy to atomize the coating; therefore, lower atomization pressures can be used, the coating viscosity remains consistent, the solids by volume are not diminished (thereby reducing risks of runs and sags), and solvent levels are maintained.

For any epoxy, using excess amounts of solvents for viscosity control is not good practice. It can result in poor application, prolonged curing, and impaired performance. Even if the contractor has accurately metered plural component equipment, or standard airless equipment fitted with in-line or pre-heaters, the product must be mixed carefully and homogeneously before it reaches the pump. It cannot be overemphasized that keeping the product in a controlled environment will greatly assist in a successful application.

The solvent to be used to clean and

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Table 5
Checkpoints for Applicators

a) Proper surface preparation

- Cleanliness of the steel substrate (contaminant removal)
- Correct type and cleanliness of the abrasive
- Dust removal by vacuum cleaning
- Appropriate blast profile with jagged anchor pattern
- Removal of sharp edges, protrusions, and heavy scale

b) Proper application techniques

- Adequate and clean spray equipment
- Proper mixing techniques
- Proper mixing—no "off ratios"
- Proper use of thinners
- Proper attention to temperature and storage of mixed paints
- Proper striping and ventilation
- Conformance to recoat window in multi-coat applications
- Proper spray technique, especially with AHC epoxies

c) Proper quality control techniques

- Strict control of substrate temperature, humidity, and ventilation during all phases of application, drying, and curing
- Strict adherence to the specified dry film thickness (dft) per coat and total dft
- Adequate curing time before service

flush out the spray pump should be compatible with the one to be used in the application. This action will prevent potential reaction or contamination from residual material in the lines and establish the working order of the equipment. Once the equipment is cleaned and inspected, it is also suggested that "off target" product spray test areas be completed before spraying the actual substrate. These tests are necessary to confirm that the proper equipment has been selected for effectively transferring the specified coating.

Equipment pressures and temperatures (if heat is used for viscosity control) should be documented when the correct spray pattern has been obtained. This is also an extremely important time to establish familiarity with the coating system, such as film build and tack-free capabilities, color hiding, and flow out, especially if the applicator does not have experience with the system specified.

Ideally, the coating should be applied when the substrate temperature is at least 5 degrees F (3 degrees C) above the dew point. Dehumidification and ventilation may be needed in the pipes or tanks during the blasting, application, and curing of

coatings. Low temperature or rapid cure does not mean one can paint a pipe or tank, internally or externally, in a snowstorm at -10 F (-23 C). What should be clarified is exactly what the low temperature or rapid cure means. The viscosity of the coating should be in a state where it can be effectively transferred. If the temperature of the coated substrate drops as low as -40 F (-40 C), the coating will eventually cure, and the performance will not be compromised, provided the temperature reaches the minimum standard required for cure.

The preferred method to determine positive cure with the MMB epoxies is time at temperature. A less favorable but acceptable test is the sandpaper test. Positive cure can be established by sanding through all coats to bare steel (using 100 to 220 grit wet or dry sandpaper) and producing a powder. No gumming will be evident on the sandpaper from cured epoxy. Another test for cure is the pencil hardness test, ASTM D 3363-74, for MMB (criterion of 3H), or Shore D or Barcol in the case of the AHC coatings.

Holiday detection of the thin-film (<20 mils dft [500 micrometers]) MMB epoxies should be conducted using low

Remember the Basics

Before starting or even awarding any coating application project, there should be a pre-job meeting with all parties concerned in attendance so that familiarity and understanding can be gained with the anticipated project. Discussions will include

- the project;
- safety issues;
- owner's requirements with respect to permits and accessibility;
- project specifications;
- order of authority pertaining to the project;
- responsibilities for necessary extras such as power, heat, light, fuel, tarps, and scaffolds;
- if and where there are hold points in the application;
- degree of acceptability for the application steps;
- dft requirements—minimums and maximums;
- monitoring and documentation of the application;
- degree of acceptability concerning aesthetics;
- cure procedures;
- holiday testing;
- repair procedures (if necessary);
- acceptance/rejection criteria; and
- special equipment per manufacturers' recommendations.

voltage (wet sponge) holiday testing equipment. Although high voltage testing can be carried out and will not damage MMB epoxies, there is always the potential of locally stressing the coating, causing burn-through, and creating a holiday. The ultra-high thick-film AHC epoxy linings should be tested at 100 volts/mil using hot spark equipment as per NACE RP 01-88-90.

Summary

The chemistry, testing, and application aspects of rapid-cure MMB epoxies (some cure to 0 F [-18 C]) and AHC epoxies (some cure to 32 F [0 C]) are critical factors in coating success. MMB and AHC epoxies have outstanding properties that make them suitable for year-round application to either the interior or exterior of steel and concrete pipes and tanks. Both of these

epoxy technologies have given excellent performance in laboratory tests and for decades have a proven track record in the petrochemical, water and wastewater, pulp and paper, and railcar industries.

MMB epoxies have low temperature cure characteristics and do not require any accelerators. They are readily applied using standard airless spray equipment.

Single-coat AHC linings are highly chemically resistant and very useful for concrete secondary containment structures. Although plural component equipment is the preferred method to apply these AHC linings, 45:1 airless pumps have been used for more than 20 years during summer and winter by preheating the product.

Project management, with capable and cooperative applicators following a good set of guidelines and use of common sense, will result in successful applications and long-term performance. □

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