RECENT DEVELOPMENTS IN EPOXY COATINGS

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ABSTRACT

A new, fast drying, surface tolerant, high-build epoxy coating offers advantages for industrial maintenance, new construction, marine and offshore coating work. Performance properties of the new coating are reviewed and compared to traditional coatings used in these applications.

INTRODUCTION

Epoxy coatings are the workhorses of the protective coatings industry. They have excellent chemical and corrosion resistance, high mechanical strength, good adhesion to a variety of substrates and a combination of other properties that have made them a material of choice for providing cost effective, long term protection on industrial, marine and offshore structures.

The major limitations of epoxy coatings are their relatively slow cure in cold climates and poor exterior color and gloss retention. The issue of color stability and chalking is typically addressed by topcoating with aliphatic polyurethane, acrylic-siloxane, epoxy-siloxane or other inherently weatherable coating (1, 2). Slow cure at low temperatures is a continuing problem. This paper briefly reviews some of the approaches used by protective coatings suppliers to address this limitation and presents information on a new epoxy coating. Application and performance property test data on the next generation of fast curing, surface tolerant epoxy coatings is discussed and compared to state-of-the-art.

BACKGROUND ON SURFACE TOLERANT COATINGS

Coatings that can be applied over damp, chemically contaminated or rusty steel, old paint and other minimally prepared substrates are described as surface tolerant. Generic types include red lead alkyd, epoxy and aluminum epoxy mastic, urethane, coal tar mastic, modified wax and grease based coatings, chlorinated rubber, modified acrylic latex, calcium sulfonate alkyd and modified vinyl chloride latex (3, 4, 5). Another category of surface tolerant coating is the "rust converter". These coatings are generally thought to provide protection by reaction with iron and the metal substrate by chelating, complex formation or passivation.

Considerable work on surface tolerant coatings has been reported in the literature and it is an area of active research for raw material suppliers and coating manufacturers. Consideration of surface tolerant coating design criteria and discussion of theoretical mechanisms by which a surface tolerant material provides corrosion protection are beyond the scope of the present paper. The subject has been reviewed and discussed extensively by Frondistou-Yannas, Huffman, Appleman, Hower and Soltz, among others (4,6,7,8,9) The coating properties and characteristics of a "good" surface tolerant coating cited most often in the literature are listed below.

- good penetration and wetting properties
- good adhesion under dry and wet conditions
- high electrical resistance to provide a barrier between anodic and cathodic sites of corrosion cells
- good barrier properties i.e., low water, oxygen and ionic permeability
- rust conversion, neutralization of chloride and sulfate salts
- high film thickness or multiple coats
- ability to minimize internal stress

In general, the epoxy types have enjoyed the most commercial success because they are user friendly and reduce the cost of surface preparation while providing excellent long-term corrosion protection. High solids, epoxy surface tolerant coatings have been available for more than 20 years. These two component coatings are based on a relatively low molecular weight liquid or solid epoxy resin component, a polyamide or polyamine component, inhibitive or barrier pigments and proprietary additives to promote flow and leveling, substrate wetting, adhesion and corrosion resistance.

Despite their apparent commercial success, the typical high solids, surface tolerant epoxy coating is relatively slow to dry at ambient temperature with dry hard times of 12 to 24 hours at 70F. Low temperature application is generally limited to 40 or 50F with dry times at these temperatures being 50 hours or more (10).

CURRENT FAST DRY, SURFACE TOLERANT EPOXY COATING TECHNOLOGY

Faster drying epoxy coatings and curing at colder temperatures have long been goals of protective coatings suppliers. Improved production rates, reduced time for job completion, as well as the ability to lower application cure conditions and extend the painting season are attractive to coating supplier, applicator, end-user and owner alike.

Protective coating suppliers have used four approaches to develop epoxy coatings with improved dry times and low temperature cure capability.

- accelerators and catalysts
- faster reacting epoxy resins
- faster reacting amine curatives
- blends and hybrids

Use of accelerator and catalyst

Formulators of epoxy coating systems have used accelerators and catalysts to improve dry times and cure characteristics since the introduction of epoxy technology more than 40 years ago. Several classes of chemicals accelerate the amine-epoxy reaction. These include tertiary amines (e.g., benzyl dimethylamine and the ubiquitous 2,4,6 tri (dimethylaminomethyl) phenol), aliphatic amines, substituted phenols (bisphenol A and nonyl phenol), organic acids (salicylic or benzoic), aliphatic alcohol's and water (11, 12, 13).

Use of these materials can compromise application and performance properties. Tertiary amines are particularly problematic. These accelerators are added to the amine curative component or are packaged as a third component and added at the job site. While ambient and low temperature dry times are generally improved, tertiary amines are water sensitive and can promote water spotting, surface blushing and subsequent intercoat adhesive failure (14). Other problems include poor color stability and an increase in film brittleness.

Faster reacting epoxy resins

Epoxy resin reactivity is influenced by the type, number and location of epoxy groups within the resin molecule. Steric factors and the presence of other reactive groups (e.g., olefin, hydroxyl and amine) also influence reaction with specific curatives(15). Epoxy resins with inherently faster reactivity have been developed by incorporation of an amine or hydroxyl group into the epoxy resin molecule. An interesting example is the hydroxymethyl group modified epoxy resin which has been reported to be several times more reactive than standard bisphenol A epoxy types (16). Epoxy resins containing other reactive groups have been used in epoxy adhesive and composite formulations to provide improved cure rates but, to date, incorporation into surface tolerant epoxy coating formulations has resulted in only modest improvement in low temperature cure characteristics.

Blends and Hybrids

Raw material suppliers and coating manufacturers have also approached the need for improved low temperature cure by blending the epoxy resin or amine curative with other resin types. For example, addition of a solid hydrocarbon resin or thermoplastic acrylic resin in solvent results in so called "snap dry" when the solvent evaporates. Another approach has been to blend resins that contain unsaturation (e.g., polyacrylates or acrylate esters such as trimethylolpropane triacrylate) with the epoxy resin (17,18). These resins or oligomers react with amine groups via the so-called Michael addition reaction to provide significant improvements in dry times. However, pot lives are much shorter using this approach and, at levels above 20% modification, chemical and corrosion resistance properties are usually compromised.

Faster reacting amine curatives

The use of inherently faster reacting amine curatives to develop improved surface tolerant epoxy coating formulations has become popular in recent years. Included in this category are polymercaptans and polysulfides, episulfides, certain types of Mannich bases, phenalkamines and modified polyamines (19). These amine curatives may be used in combination with standard polyamides and amidoamines or by themselves as hardeners for the epoxy resin component. Use of this approach has enabled coating manufacturers to develop surface tolerant systems with improved dry times and low temperature cure capability down to 20F.

A discussion of the relative merits of the various amine chemistries is beyond the scope of the current paper. In general, two types of fast reacting amines have gained considerable commercial acceptance; those based on mercaptan-modified polyamide and those based on phenalkamine. Epoxy coatings based on these amine curatives have good low temperature cure characteristics, excellent adhesion to rusty steel, old paint and other compromised substrates and have an outstanding track record for corrosion protection in a variety of harsh industrial and marine service conditions.

Limitations of current faster reacting amine curatives

A decided disadvantage of the surface tolerant epoxy coating based on mercaptan-modified polyamide, of course, is its odor. Worker complaints during application are frequent. Other disadvantages include poor color stability and a tendency to blush in high humidity environments.

Surface tolerant coatings based on phenalkamine cured epoxy, particularly those based on cashew nut shell liquid, have very poor in-can and as-applied color stability. Phenalkamines with improved in-can color stability have recently become available, however, applications which require good exterior gloss retention and color stability still require application of a light stable topcoat. Another disadvantage of the phenalkamine cured epoxy is limited recoat and topcoat time. Typically, these coatings require solvent wiping, sand blasting or water jetting after 30 days cure for recoating and seven days cure for topcoating to ensure good adhesion and adequate long term performance. Further, the typical volume solids and VOC of these coatings are only about 68% and 292 grams/liter, respectively.

NEW FAST REACTING SURFACE TOLERANT COATING

A new generation of fast reacting, surface tolerant epoxy coating has been developed that offers improvements compared to state-of-the-art. The coating is based on unique epoxy resin/modified polyamine -polyamide chemistry and proprietary formulation technology.

As shown in Table 1, the coating has very high volume solids and will meet the new VOC limit of 250 g/l established by California SCAQMD Rule 1113 starting in 2002. Other characteristics include fast dry to recoat and ease of application by brush, roll and spray.

Table 1.
Properties of New, Fast Reacting Surface Tolerant Coating

Components	2
Appearance	semigloss
VOC	1.4 lb./gal (168g/l)
Volume Solids	88%
Recommended DFT	4-8 mils
Theoretical Coverage at 5 mils	266 sq. ft/gal
Application method	brush, roll, spray
Pot life at 70F	1.5 hours
Dry times at 70F	
- touch	2.0 hours
- through	4.5 hours
- recoat, min	3.0 hours
- recoat, max	45+ days

Evaluation

An extensive evaluation of the new, fast drying surface tolerant epoxy coating was conducted. The two commercially available fast dry, surface tolerant coatings previously mentioned were used as benchmarks. They will be referred to as follows:

- mercaptan-modified polyamide cured epoxy and
- phenalkamine cured epoxy

Sample Preparation

All application and performance properties were conducted on white, TiO_2 pigmented formulations applied to the appropriate substrate using a DeVilbiss conventional air spray gun. Except for dry time studies, coated panels were allowed to cure for 14 days at 70F and 50% relative humidity before testing.

Application Characteristics and Dry Times

ASTM-D1640dry through times of the three coating systems were measured at 20F, 32F, 50F and 70F. The appearance of all test panels after curing was excellent with no evidence of carbamate formation or blushing. Test results are reported in Table 2.

The new coating compares favorably to both the phenalkamine cured epoxy and mercaptan-modified polyamide cured epoxy at temperatures from 32F to 70F. The phenalkamine-cured epoxy is slightly faster at 20F.

Low temperature cure kinetics were also studied using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Weinmann, Dangayach and Smith (among others) have used this technique to determine extent of reaction and cure rate of epoxy/amine binder systems (17). The results of this study can be seen in Figure 1, Figure 2 and Figure 3. These graphs show the time to reach 80% of full cure at temperatures from 40F to 120F. Cure rates in this temperature range are favorable for the new, fast reacting surface tolerant epoxy coating system.

Recoat and Topcoat Times

Fast recoat and topcoat times allow subsequent coats to be applied quickly and usually result in increased productivity. Long or unlimited maximum recoat and topcoat times can minimize the amount of surface preparation required to achieve adequate adhesion of the next coat and can significantly reduce maintenance painting costs.

Recoat and topcoat times are shown in Table 2. Minimum recoat and topcoat times for the new, fast reacting surface tolerant epoxy coating system are better than either of the other two coating systems. Although the new coating has faster dry to recoat and topcoat times, preliminary data indicates that it has longer maximum recoat and topcoat times. For example, maximum recoat time at 70F for the new coating is at least 45 days while the other coating systems are limited to 14 days for the marcaptan-modified polyamide and 30 days for the phenalkamine system. Maximum topcoat times are also favorable for the new coating.

Odor Evaluation

Mercaptan-modified epoxy coating systems have a noxious odor during application and the early stages of cure. Reodorants or masking agents are often used by coating formulators to mitigate the smell, however, these materials may compromise certain performance properties.

Odor is a difficult characteristic to quantify and is inherently subjective. A sensory panel of six people was formed to address this problem. The panel evaluated the relative odor of the three coating systems compared to a standard polyamide cured epoxy according to guidelines recommended in ASTM D-6165. Relative odor ratings were conducted on liquid coating mixtures and spray applied panels after 16 hours cure using the same quantities, containers, test panels and exposure conditions.

In this evaluation, the standard polyamide epoxy was assigned a value of three. Lower numbers indicate less odor and higher numbers indicate more odor. As shown in Table 3, the new, fast reacting surface tolerant coating had less odor than any of the other coatings.

Table 3. Odor Evaluation

Epoxy Coating System	Mixed Coatings	Spray-Applied
Standard polyamide	3	3
Mercaptan-modified polyamide	5	4
Phenalkamine	4	3
New Modified Polyamine-Polyamide	2	2

1 = much less odor 4 = more odor
2 = less odor 5 = much more odor
3 = standard

Accelerated Weathering –Gloss and Color Stability

QUV-B Accelerated Weathering tests were conducted on Ti0$_2$ pigmented coatings. The data is presented in Table 4. Of note, the phenalkamine coating changed color from white to a light yellow-brown within 24 hours of application and continued to yellow in the QUV chamber. As previously mentioned, this problem is well known and has limited the use of phenalkamine based coatings.

As expected, all of the coatings lost most of their gloss after only a few days exposure. CIE L·a·b color measurements were taken initially and after exposure to QUV-B using a Minolta Spectramatch color computer. The Delta E total color change data shows that the new coating has significantly better resistance to discoloration from exposure to UV light than the benchmark coating systems.

Corrosion Resistance Testing

Salt fog, Cleveland humidity and Prohesion test results are compared in Table 5. Review of this data indicates that the new, fast reacting surface tolerant coating has comparable or better corrosion resistance over blast cleaned steel (SP-10) and power tool cleaned rusted steel (SP-3) compared to the mercaptan-modofied polyamide cured epoxy and the phenalkamine cured epoxy coatings.

Low moisture vapor transmission rate (MVT) has been correlated with good corrosion resistance and is thought to be one of the mechanisms by which the so-called barrier coatings provide corrosion protection. MVT data, shown in Table 6, is favorable for the new coating system.

Adhesion

Good adhesion has been shown to be of significant importance for long term corrosion protection over compromised substrates and sand blasted steel. Elcometer adhesion to SP-10 Steel and SP-3 Rusted Steel is compared in Table 7. All three coatings had good adhesion i.e., failure was cohesive within the epoxy coating. However, the new, fast reacting surface tolerant epoxy had greater adhesion to both sandblasted and rusted steel.

Impact Resistance and Conical Mandrel Elongation

Impact resistance and conical mandrel elongation test results are compared in Table 8. The data shows all three coating systems have comparable flexibility.

Chemical Resistance Testing

Table 9 compares the resistance of the three coating systems after twenty-four hour exposure to a number of chemicals. The data indicates all of the coating systems have good resistance to splash and spillage of a broad range of chemicals. Of interest, the new surface tolerant epoxy coating has improved resistance to sulfuric, hydrochloric and acetic acids.

Preliminary results of immersion testing are also positive. After six months exposure, test panels of the new fast reacting surface tolerant epoxy show no evidence of blistering in fresh and salt water as well as a number of crude and refined petroleum products.

EVALUATION / TEST RESULTS SUMMARY

Analysis of the laboratory application and performance property test data indicates the new fast reacting, surface tolerant epoxy coating represents an incremental improvement in state-of-the-art.

The coating was found to have the following important properties and characteristics:

- very high solids and low VOC
- complies with SCAQMD Rule 1113 and National AIM regulations.
- very fast dry times and good low temperature cure.
- improved recoat / topcoat window
- corrosion resistance over blast-cleaned steel (SP-10) and power tool-cleaned rusted steel (SP-10) better than industry benchmark coatings
- excellent adhesion to SP-3 and SP-10 prepared steel.
- good resistance to chemical splash and spill with better acid resistance than industry benchmark coatings.
- less odor and better color stability than industry benchmark coatings.

CONCLUSION

Some of the approaches taken by coating suppliers to develop fast reacting, surface tolerant epoxy coatings with good low temperature cure characteristics were reviewed. In an effort to address the limitations of standard benchmark surface tolerant coatings, a new generation of fast reacting, surface tolerant epoxy coatings was introduced. Application and performance property test results indicate the new coating has improvements in corrosion resistance, ambient and low temperature dry times, recoatability, odor and color stability.

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Tanle 3. Comparison of Dry Times (ASTM D-1640) and Recoating / Topcoating Times

Coating Description	Mercaptan-Modified Polyamide Cured Epoxy	Phenalkamine Cured Epoxy	Modified Polyamine–Polyamide Cured Epoxy
Dry Times at 70F			
• touch	2 hours	3 hours	2 hours
• through	4.5 hours	10 hours	4.5 hours
• recoat/topcoat, min.	3.5/3.5 hours	4/4 hours	3/3 hours
• recoat, maximum	14 days	30 days	45+ days
• topcoat, maximum	7 days	5 days	14 days
Dry Times at 50F			
• touch	8 hours	12 hours	8 hours
• through	13 hours	22 hours	13 hours
• recoat / topcoat, min	10/10 hours	8/8 hours	6/6 hours
Dry Times at 32F			
• touch	24 hours	29 hours	24 hours
• through	38 hours	45 hours	38 hours
Dry Times at 20F			
• touch	48 hours	48 hours	48 hours
• through	96 hours	72 hours	96 hours

Table 4. Accelerated Weathering Test Results (ASTM G-53, QUV-B) – Color and Gloss Retention

Coating Description	Mercaptan-Modified Polyamide Cured Epoxy	Phenalkamine Cured Epoxy	Modified Polyamine–Polyamide Cured Epoxy
60 degree gloss			
• initial	63	25	60
• 2 days	7	18	19
• 7 days	4	3	4
Delta E			
• 2 days	13.9	16.3	9.2
• 7 days	12.5	10.8	7.7

Table 6. Moisture Vapor Transmission Rate – Mocon Permean (ASTM F-1249)

Coating Description	Mercaptan-Modified Polyamide Cured Epoxy	Phenalkamine Cured Epoxy	Modified Polyamine–Polyamide Cured Epoxy
Moisture Vapor Transmission Rate (grams/ m^2/day)	8.1	5.9	5.1
Specific Permeability (mg*mm / cm^2 / day)	0.143	0.100	0.077

Table 5. Corrosion Resistance Test Results

Coating Description	Mercaptan-Modified Polyamide Cured Epoxy	Phenalkamine Cured Epoxy	Modified Polyamine-Polyamide Cured Epoxy
Salt Fog Resistance – 3000 hours (ASTM B-117)			
Steel – SP10 - 6 mils			
Face Blistering	8 few	None	None
Face Rust	10	10	10
Scribe Performance	8	6	9
Rust Steel-SP3- 6 mils			
Face Blistering	9	10	10
Face Rust	4, 8 dense in patch	6, 8 med. in patch	8 few in patch
Scribe Performance	9	9	9
Prohesion Testing - 3000 Hours (ASTM G85-A5)			
Steel – SP10 – 6 mils			
Face Rust	10	10	10
Face Blistering	None	None	None
Scribe Performance	5	6	6
Rust Steel-SP3– 6 mils			
Face Rust	10	10	10
Face Blistering	None	None	None
Scribe Performance	10	9	10
Cleveland Humidity Resistance - 2000 Hours (ASTM D-4585)			
Steel – SP10 - 6 mils			
Face Rust	10	10	10
Face Blistering	8 few in patch	None	None
Rust Steel–SP3–6 mils			
Face Rust	10	10	10
Face Blistering	8 few	8 med .dense	8 few in patch

Table 7 Elcometer Adhesion Test Results (ASTM D-4541)

New Modified Polyamine-Polyamide Cured Epoxy	1300 psi	500 psi
Phenalkamine Cured Epoxy	800 psi	400 psi
Mercaptan-Modified Polyamide Epoxy	900 psi	400 psi

Table 8. Impact Resistance and Conical Mandrel Elongation

Test Method	Direct / Reverse Impact Resistance (ASTM D-2794)	Conical Mandrel % Elongation (ASTM D-522)
New Modified Polyamine-Polyamide Cured Epoxy	24 / <10 in. lbs.	6%
Phenalkamine Cured Epoxy	22 / <10 in. lbs	6%
Mercaptan-Modified Polyamide Epoxy	24 / <10 in. lbs	13%

Table 9. Chemical Resistance – Twenty-Four Hour Spot Tests (ASTM D-1308)

Test Chemical	Mercaptan-Modified Polyamide Cured Epoxy	Phenalkamine Cured Epoxy	Modified Polyamine–Polyamide Cured Epoxy
Sodium Hydroxide, 50%	10	10	10
Ammonium Hydroxide, conc.	10	10	10
Hydrochloric Acid, conc.	4	4	9
Sulfuric Acid, conc.	4	4	5
Sulfuric Acid, 50%	3	6	10
Phosphoric Acid, conc.	3	3	33
Phosphoric Acid, 50%	0	0	2
Acetic Acid. conc.	0	0	0
Acetic Acid, 5%	2	9	8
Acetone	4	4	4
Ethyl Alcohol, 95%	4	4	4
Phenol, 85%	0	0	0
Cumene	0	0	0
NaOCl, 5%	7	7	7

10 = no change
8 = slight change
6 = definite change
4 = major change
2 = partial failure
0 = complete failure