



Formulating High-Performance Waterborne Epoxy Coatings

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Abstract

This paper deals with two myths. The first is that waterborne epoxy coatings cannot achieve the performance of solvent-based epoxy coatings. The second myth is that coating formulators often believe that they can formulate waterborne epoxy coatings just like they do other waterborne systems. In fact, the tools required to formulate waterborne epoxy coatings can be fairly unique and very specific. Experience has shown that formulators, who deviate from these specific tools, often achieve poor coating performance. This paper discusses the many preferred approaches and specific recommendations to formulate truly high-performance waterborne epoxy coatings.

Important Note

We have repeatedly found that, without very specific material recommendations, formulators are often unsuccessful in formulating high-performance waterborne epoxy coatings. They unknowingly select pigments, additives, etc., which may give great performance in other coatings, but which give sub-optimal performance in these waterborne epoxy coatings. This reinforces the myth that high-performance waterborne epoxy coatings cannot be formulated. We have structured this paper to emphasize preferred formulating concepts, and to identify specific materials (pigments, fillers, additives, etc.) which we or others have found to work well in high-performance systems. We do this with the understanding that the materials which we cite are probably not the only ones that will give high-performance coatings. However, at this time, these are the only ones that we are aware that do so. We trust that the readers of this paper will be able to use this information constructively, and may well find alternative materials which will also give high-performance coatings.

Background

Epoxy resins (based on the diglycidyl ether of bisphenol A) were commercialized nearly 60 years ago. It was quickly determined that they are useful in formulating direct-to-metal coatings with excellent adhesion, chemical resistance, and corrosion resistance. As such, epoxy based coatings have been used extensively as high-performance primers for metal substrates. As an example, virtually every automobile manufactured in the world today is first coated with an epoxy based primer which provides outstanding corrosion resistance. The most widely used epoxy resins, by far, are still those based on bisphenol A.

Historically, most high-performance epoxy primers, especially those used in ambient cure applications, are based on solvent based epoxy resins. So, although they provide excellent performance, they have the disadvantage of relatively high VOC content.

About 30 years ago, chemists began formulating waterborne epoxy resins and curing agents which could be formulated at significantly lower VOC levels than solvent based epoxy coatings. The technical problem which arises is that bisphenol A epoxy resins are rather hydrophobic, and do not readily disperse in water. Therefore,

surfactants were developed which would disperse these hydrophobic resins in water. The first generation (Type 1) waterborne epoxy resins are liquid epoxy resins dispersed in water using appropriate surfactants. Curing agents are generally water soluble amines. Often the curing agents are salted with an acid to enhance water solubility. The use of surfactants and water soluble amines result in coating films which are relatively hydrophilic. As such, they do not provide good corrosion resistance when applied to metallic substrates. However, they are very useful when applied to non-metallic substrates, such as flooring or masonry. The weakness of their poor hydrophobicity is not evident in these applications. Coatings formulated with these materials can achieve zero VOC.

The next generation (Type 2) waterborne resins are dispersions of solid epoxy resins in water. These generally require the use of cosolvents as coalescing aids in the film formation process, so very low VOC levels are more difficult to achieve. Water soluble amines are generally used as curing agents. The performance of the Type 2 system is improved over Type 1. This is due largely to lower curing agent demand by the higher molecular weight solid resin. The curing agent is the most hydrophilic part of the system. However, the corrosion resistance is still weak (compared to

solvent borne epoxy coatings), so they could only be used for light-duty metal primers or for non-metallic substrates.

The next generation (Type 3) is comprised of a liquid or solid epoxy dispersion, and a carboxyl-functional acrylic dispersion. This kind of system provides improved weathering characteristics by being more resistant to yellowing and chalking than standard epoxy systems. However, these coatings do not exhibit the excellent corrosion resistance when applied to metal substrates, so they are most useful for topcoats.

Type 4 waterborne epoxies are liquid or liquid emulsions cured with amine dispersions. These give good performance on floors or masonry, but give weak performance on metal.

For 25 years, waterborne epoxy technology was represented by one or more of these system types. None of them give corrosion protection to metal as good as solvent based epoxy coatings. So the myth developed that it is not possible to formulate waterborne epoxy coatings that will perform as well as solvent based systems. The fact that hydrophilic surfactants are required to disperse epoxy resins and curing agents in water provided technical justification for this myth.

Type 5 Epoxy System

The latest generation of waterborne epoxy was developed using a "1-type" (epoxy equivalent weight of about 500–600) solid epoxy dispersion, and a hydrophobic amine adduct curing agent. Both components utilize a proprietary, non-ionic surfactant that is pre-reacted into the epoxy and amine components. Table 1 gives an example of a waterborne epoxy using this approach.

Table 1. Typical Properties of a Type 5 Waterborne Epoxy Resin Dispersion

Name	EPI-REZ™ 6520-WH-53
Description	Modified 1-type
Epoxy equivalent weight (based on solids)	500–600
Viscosity (Brookfield, 25°C, cP)	1,000–6,000
Solids (wt. %)	52.0–54.5
Weight per gallon (lb.)	9.0
Appearance	Milky white, opaque
VOC solvent	<4% propylene glycol methyl ether

Table 2. Typical Properties of a Type 5 Curing Agent Dispersion

Name	EPIKURE™ 6870-W-53
Description	Modified polyamine adduct
Amine H equivalent weight (on solids)	225
Viscosity (Brookfield, 25°C, cP)	8,000
Solids (wt. %)	53.0
Weight per gallon (lb.)	9.1
Appearance	Milky white, opaque
VOC solvent	None

Table 3. Starting Point Formulation No. 1700, Waterborne White Epoxy Primer			
Material	Supplier	Pounds	Gallons
Part A			
EPI-REZ 6520-WH-53	Hexion Specialty Chemicals	300.0	33.33
Dowanol PPh	Dow Chemical Co.	30.6	3.47
EFKA 2526 Defoamer	Elementis	3.0	0.35
Ti-Pure R-960	DuPont	100.0	3.10
10 ES Wollastocoat	NYCO Minerals Inc.	100.0	4.12
Sparmite A Barytes	Elementis Pigments Inc.	67.0	1.83
Halox SW-111	HALOX Pigments	94.7	3.98
Wet Ground Mica, 325 mesh	Franklin Industrial Minerals	7.0	0.30
<i>High speed disperse to 5–6 Hegman. Reduce speed and add:</i>			
EPI-REZ 6520-WH-53	Hexion Specialty Chemicals	147.8	16.42
CoatOSil® 1770	Hexion	8.6	0.98
DI Water		101.2	12.12
Total Part A		959.9	80.0
Part B			
EPIKURE 6870-W-53	Hexion Specialty Chemicals	180.0	19.78
Raybo 60	Raybo Chemical Co.	2.0	0.22
Total Part B		182.0	20.00
Total Parts A & B		1,142.5	100.00

Table 4. Characteristics of Starting Point Formulation No. 1700	
Mix ratio by volume	4:1
Total weight solids (%)	62.7
Total volume solids (%)	48.9
PVC (%)	27.2
VOC (lb./gal.)	0.82
VOC (g/l)	98.0
Induction time	None
Pot life (hours)	5–6

High-performance Waterborne Epoxy Example

Table 5 compares the performance of a Type 5 waterborne epoxy enamel with that of a conventional solvent borne epoxy-polyamide enamel based on a solid epoxy and a polyamide.

The Type 5 waterborne epoxy gives faster dry, faster hardness development, better salt spray and lower VOC than the solvent based control. Other characteristics, such as impact performance, water immersion resistance, and MEK double rubs are equivalent.

The problem with many waterborne epoxy coatings is that they do not have a detectable end of pot life. They stay fluid, so the painter may continue to use the mixed paint beyond the useful pot life. The gloss and other performance properties are significantly degraded if it is used beyond the pot life. The Type 5 waterborne epoxy has a visible end of pot life. The viscosity rises dramatically, and the painter should stop application at that point. The gloss remains level throughout the pot life, and does not drop until the viscosity begins to rise. Figure 1 shows these results, after reduction to spray viscosity.

Table 5. Performance Comparison of White Enamels		
Characteristic	Type 5 Waterborne Epoxy	Solvent Based Epoxy
VOC (lb./gal.)	1.02	3.7
Dry time (hr., cotton free)	4	8.5
24 hr. pencil hardness	2B	4B
14 day pencil hardness	H	F
Impact (dir./rev., in-lb)	140/140	160/160
1000 hr. salt spray	8F–6F	6F
Water immersion (days @ 25°C)	>250	>250
MEK double rubs	>300	>300

Figure 1. Discernible End of Pot Life

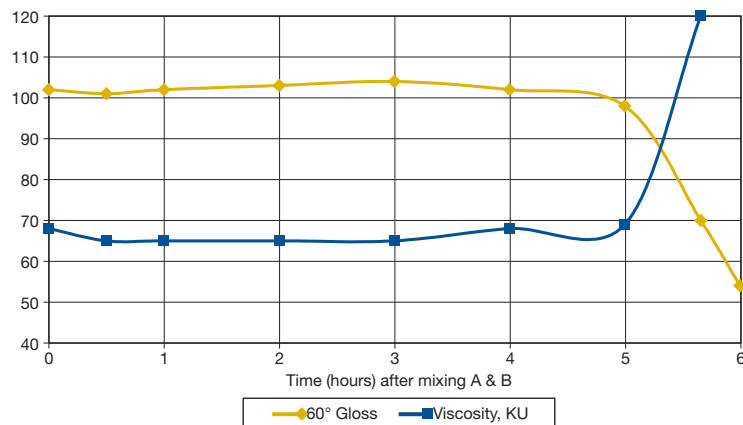


Figure 2 compares the 2000 hour salt spray performance for the Type 5 epoxy with that of a conventional solvent borne coating based on a solid epoxy resin cured with a polyamide. This later system has given excellent corrosion protection for over 40 years. Both coatings were applied to cold rolled steel at 3 mils dry film, and were fully cured. Clearly, the waterborne coating is a high-performance system that outperforms the solvent borne control.

There are many factors of coating formulation that influence the performance of waterborne epoxies. If high levels of performance are desired, then techniques used to formulate other waterborne coatings, such as acrylics, cannot be used with waterborne epoxies. If the Type 5 waterborne epoxy is not formulated properly, then poor performance will result. The remainder of this paper will discuss these factors and the preferred approaches for high-performance waterborne epoxy coatings.

Stoichiometry Effects

Stoichiometry is the ratio of amine hydrogen to epoxy in a particular formulation. As a general rule, one would formulate at a stoichiometric ratio of 1:1. This tends to maximize crosslink density. A 1:1 ratio is simply calculated using the equivalent weights of the resin and curing agent. To calculate the parts by weight curing agent to use per 100 parts of resin (phr), on a solids basis, one calculates:

$$\text{PHR curing agent} = \left(\frac{\text{amine H eq. wt.}}{\text{epoxy eq. wt.}} \right) \times 100$$

For the resin in Table 1 and the curing agent in Table 2, one gets:

$$\text{phr curing agent} = \left(\frac{225}{550} \right) \times 100 = 41$$

41 grams of curing agent at 53% solids is 77.4 grams curing agent solution. 100 grams of epoxy at 53% solids is 188.8. So a theoretical 1:1 ratio for this system would be a ratio of 188.8 parts by weight of resin dispersion and 77.4 parts by weight of curing agent, or any equivalent ratio (e.g., about 40 parts curing agent dispersion to 100 parts epoxy dispersion by weight).

Figure 2. 2000 Hour Salt Spray



Solvent borne epoxy/polyamide

Type 5 waterborne epoxy

Figure 3 shows some of the effects of increasing the curing agent level in a particular formulation.

Figure 3a. Effects of Increasing Curing Agent Content

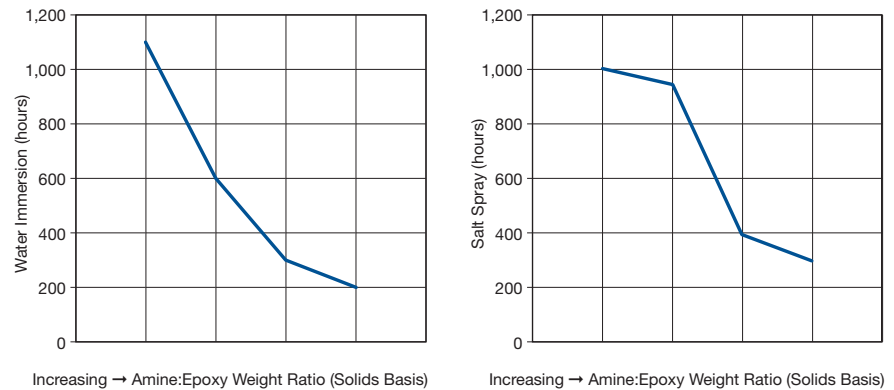
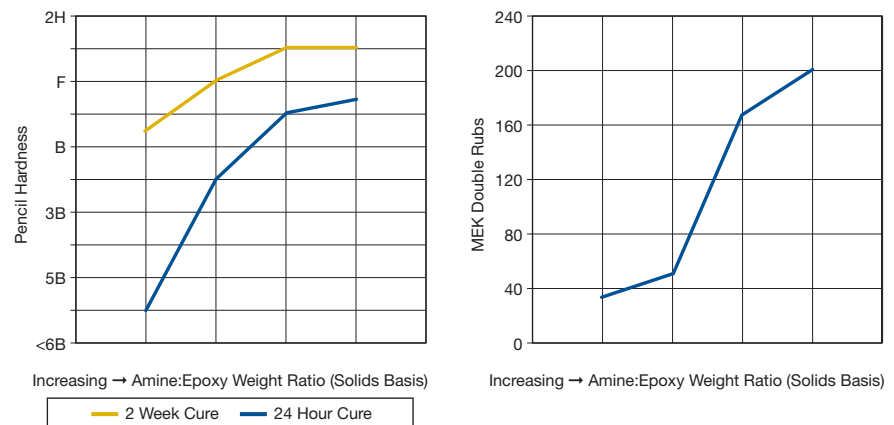


Figure 3b. Effects of Increasing Curing Agent Content



White enamels based on the Type 5 waterborne epoxy were evaluated at stoichiometries from 65% to 130% of the theoretical amine content. The results are provided in Table 6. In general, increasing the curing agent ratio resulted in faster dry times, improved twenty-four-hour hardness development, impact resistance, and solvent resistance (MIBK and MEK). Water immersion and salt spray resistances are better at lower amine ratios. These observations fit with the trends in Table 6 but it is important to note that the best overall balance of properties appears to be at 100% stoichiometry (+/- about 15%). For this reason, the Type 5 binder system is typically formulated at 1:1 stoichiometry. If a formulation needs to be further optimized for better performance in a specific test then adjusting the epoxy/amine stoichiometry can be utilized to achieve the desired results.

Table 6. Performance of White Enamels at Various Stoichiometries					
Property	65%	85%	100%	115%	130%
Calculated VOC,					
lb./gal.	1.07	1.03	0.99	0.96	0.94
gm/liter	128	123	119	116	112
Tack-free dry time, hr.	5.75	4.0	3.0	2.0	2.5
Thru-dry dry time, hr.	8.5	8.0	8.0	4.0	8.0
24 hr. pencil hardness	5B	2B	HB	HB	HB
14 day pencil hardness	F	H	H	H	H
Impact (Dir./Rev.) in.-lb.	24/4	36/4	36/12	52/36	56/16
MEK double-rubs	149	308	165	337	365
MIBK resistance, min.	15	35	45	>60	>60
Water immersion (25°C), day	>51	>51	>51	>51	37
—ASTM blister rating	10	10	10	10	8M
Salt spray, hr.	960	960	960	432	264
Undercutting, mm	2.0	2.5	5.5	5.0	5.0
ASTM field blisters	8F	8F	6F-6M	4M	2M

The amine curing agent is the most hydrophilic part of the formulation, so changing the amount of amine will influence many performance properties of the system. These affects are summarized in Table 7.

Table 7. Epoxy to Amine Ratio Affects on Performance	
<p>Increasing the epoxy relative to curing agent gives improved:</p> <ul style="list-style-type: none"> ▪ Pot life ▪ Acid resistance ▪ Water resistance ▪ Humidity resistance ▪ Corrosion resistance 	<p>Increasing the curing agent relative to epoxy gives improved:</p> <ul style="list-style-type: none"> ▪ Cure rate ▪ Gloss ▪ Adhesion ▪ Solvent resistance ▪ Stain resistance

Pot Life

These are reactive, two-part systems. After the parts are mixed, they begin reacting immediately. The painter has a limited amount of time to apply the coating, before the reaction reaches some critical level. As one approaches the end of pot life of a waterborne epoxy, the following usually happens:

- Viscosity increases dramatically
- Gloss decreases
- Cure hardness may decrease

Table 8. Factors Affecting Pot Life	
As the variable below increases...	Pot life...
Epoxy/curing agent ratio	Increases
Acid addition to curing agent	Increases
Temperature	Decreases
Catalyst level	Decreases
Initial viscosity	Decreases
Solids	Decreases

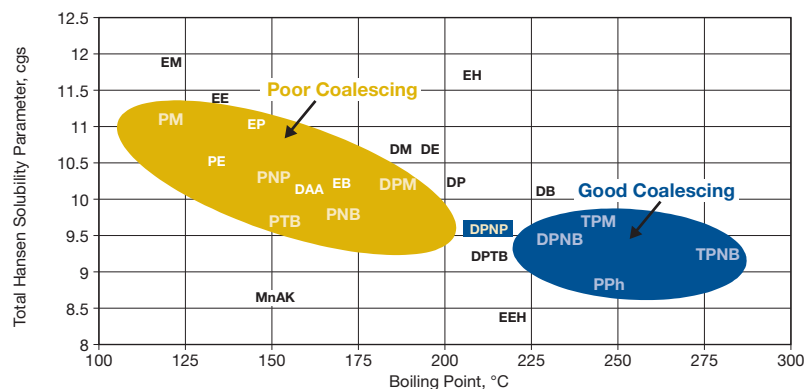
Cosolvents

Cosolvents fill a number of important functions in a waterborne epoxy coating, including:

- Coalescing aids
- Freeze-thaw stabilizers
- Leveling and flow agents
- Pigment wetters
- Foam control

Cosolvents can affect performance in areas such as dry time, gloss, hardness development, and other final film properties. Glycol ethers are the most versatile. Figure 4 summarizes the relative effectiveness of glycol ethers. These results suggest that the best coalescing aids are high boiling solvents with relatively low solubility parameters. The higher effectiveness of high boiling cosolvents is logical, because they evaporate slowly and stay in the film longer. Ethylene glycol ethers are suitable. Propylene glycol ethers are preferred for their non-HAP status. Diacetone alcohol is a useful cosolvent that can improve pigment wetting, reduce viscosity, and increase gloss. Other ketones are normally not used because of odor and hydrophobicity. Alcohols can be used to improve substrate wetting, speed dry time, and contribute to good stability. However, alcohols can also decrease flash point. Aromatics can be used, but they are strongly hydrophobic, so they partition mostly to the resin particles. They swell the resin particles and affect rheology. However, aromatics can improve gloss, stability, and ease of application. Glycol ether acetates are generally not used. When added to the curing agent, they can hydrolyze to give acetic acid which salts the amine and increases pot life.

Figure 4. Effectiveness of Glycol Ethers as Coalescing Aids



Cosolvents that are most commonly used in waterborne epoxy coatings include (with abbreviation):

- propylene glycol monomethyl ether (PM)
- propylene glycol propyl ether (PnP)
- dipropylene glycol n-butyl ether (DPnB)
- propylene glycol phenyl ether (PPh)
- tripropylene glycol n-butyl ether (TPnB)
- ethylene glycol propyl ether (EP)
- ethylene glycol butyl ether (EB)
- diacetone alcohol (DAA)
- dipropylene glycol methyl ether (DPM)

Gloss enamels based on the Type 5 binder system seem to offer the best balance of properties when a 1:1 (by weight) blend of propylene glycol phenol ether (PPh) and dipropylene glycol n-butyl ether (DPnB) is used in the formulation. Waterborne primers seem to work best with propylene glycol phenol ether (PPh)—assuming there is not a high gloss requirement. As a sole solvent, DPnB evaporates faster than PPh; however, its greater water solubility and lower azeotrope ratio result in slower release of DPnB from WB coatings relative to PPh.

When cosolvents are added to resin dispersions, they partition between the water-phase and the resin-phase but this partitioning is a relatively slow, dynamic process. For this reason, if a formulator wants to measure final component viscosity after dispersing pigments or stability testing at elevated temperatures (greater than 25°C), it is important to equilibrate the component, at least overnight but more preferably, for a minimum of twenty-four hours. Additionally, if one is making viscosity adjustments with cosolvents, one should allow sufficient time to allow the cosolvent to fully equilibrate in the formulation. For example, there have been instances where a cosolvent was added to lower component viscosity. The adjustment initially worked but twenty-four hours later, the viscosity of the component actually increased. The reason for this behavior is that at equilibrium, the cosolvent preferred to exist predominantly inside the resin particle. This caused the resin particles to swell and ultimately, increased the component's viscosity.

Freeze-Thaw Resistance

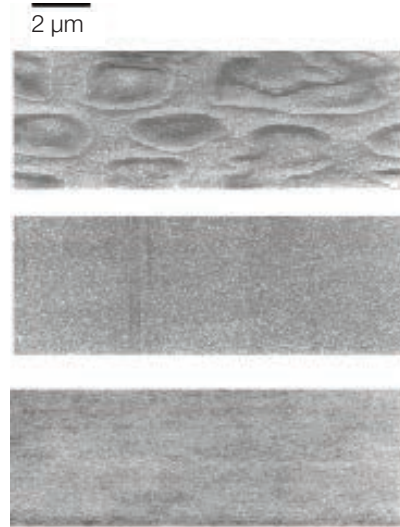
Exposing waterborne epoxies to temperatures below 30°F can cause freezing which will destabilize the dispersion. Freezing will generally cause a significant increase in viscosity. This effect may be reversible, and the dispersion will recover when it is warmed. Or the effect may be permanent, and the dispersion will not recover, and may not be useful. This typically happens when the material is exposed to low temperatures around 20°F or less. So waterborne materials and formulated products should be protected from freezing.

Formulating with cosolvents such as glycol ethers (like ethylene glycol monomethyl ether) or alcohols (like methanol) reduce the freezing point and promote recovery of frozen material. Using these cosolvents at 25–30% of volatiles generally provides resistance to 1–3 freeze-thaw cycles. In the Type 5 system, a 1:1 blend of diacetone alcohol (DAA) and propylene glycol n-butyl ether (PnB) works well for freeze-thaw resistance.

Cosolvent Formulating Tips

- Preferably, add cosolvents to the epoxy component, rather than the curing agent.
- If necessary, limit cosolvent additions to the curing agent component to 4% by weight (higher levels will destabilize the curing agent).
- Use water, or completely water soluble cosolvents in the curing agent side.
- Freeze-thaw stability can be enhanced by replacing some tail solvent with a 1:1 blend of DAA/PnB.
- Use propylene glycol phenyl ether as the tail solvent for faster recoatability or quicker return to service.

Figure 5. Coalescence Comparison



Coalescence

Waterborne epoxies are complex heterogeneous systems. A Type 5 system contains epoxy resin particles, curing agent particles, and a continuous aqueous phase. At the point of film formation, the epoxy particles and curing agent particles must coalesce so that proper cure can occur. Figure 5 shows photomicrographs of three different epoxy systems. The first picture is of a Type 2 waterborne epoxy. It shows clearly discernable regions. This morphology is interpreted to be caused by incomplete coalescence which results in regions that are epoxy rich, and regions that are epoxy poor. This is probably caused by the fact that as coalescence occurs, reaction between the components also occurs which increases molecular weight and viscosity, thus slowing and stopping full coalescence. This poor coalescence is also reflected in a relatively high surface roughness for this sample. The second picture shows a Type 5 system. There are no discernable regions, and there is minimal surface roughness. This indicates that full coalescence is achieved with this Type 5 epoxy. The third picture is of a solvent borne epoxy control, which is homogeneous when applied. This shows no regions or surface roughness like the Type 5 system.

Type 2 System

Epoxy dispersion combined with water-soluble amine

Avg. surface roughness = 25X

Type 5 System

Epoxy dispersion combined with curing agent dispersion

Avg. surface roughness = 1.25X

SB Epoxy

1-Type epoxy combined with standard high viscosity polyamide

Avg. surface roughness = 1X

As noted above, coalescence of waterborne epoxies is enhanced by the use of cosolvents. However, liquid epoxy resins or epoxy modifiers can also be used to achieve coalescence. This approach will generally improve solids and decrease VOC, as well as improve gloss, mixing ratios, and visible end of pot life. Materials that have been found to be useful in this regard include:

- diglycidyl ether of bisphenol A (e.g., EPON™ 828)
- diglycidyl ether of hydrogenated bisphenol A (e.g., EPONEX™ 1510)
- glycidyl neodecanoate (e.g., CARDURA™ E10P)

The glycidyl neodecanoate has the lowest viscosity of these modifiers, and is the easiest to incorporate into a waterborne epoxy. It also gives the best performance with improved leveling, gloss, mar resistance, and early water resistance. About 2.6 parts by weight glycidyl neodecanoate to 100 parts epoxy dispersion works well.

How to Improve Coalescence

- Formulate a little rich in epoxy binder
- Formulate a little high in VOC
- Use a balance of propylene glycol methyl ether or propylene glycol phenyl ether with dipropylene glycol n-butyl ether to improve gloss, pot life, and viscosity
- Use a liquid epoxy resin or glycidyl neodecanoate (preferred) to modify epoxy dispersion

Defoamers

Defoamers are required to suppress foam generation during manufacture, filling, tinting, and application of the paint. The best options are found empirically. It must be established that the defoamer will be effective throughout the desired shelf-life of the product.

The formulator must carefully select the defoamer and optimize the level to avoid problems such as:

- Pigment flocculation
- Poor color acceptance
- Poor inter-coat adhesion
- Surface defects like cratering or fish eyes
- Water sensitivity

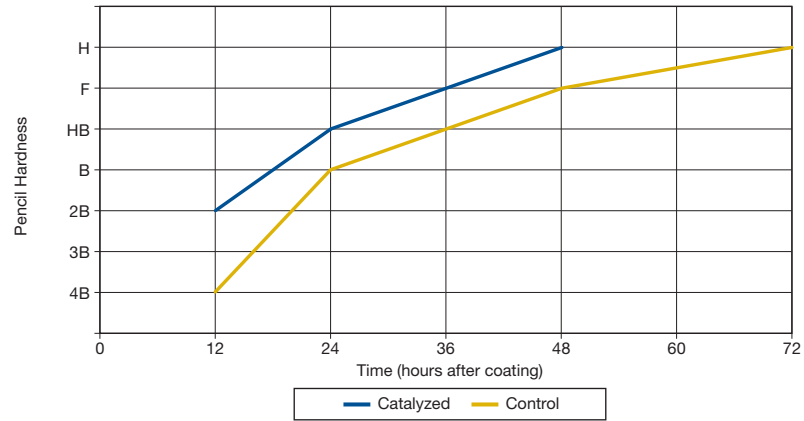
Notionally, a level of about 0.5% by volume may be used, but this must be carefully evaluated and verified for each formulation. It has been found that most defoamers are most effective if a portion is put into the grind, and the remainder is put into the let-down. Generically, effective defoamers are usually either silicone based or oil based. Excellent results have been obtained in a Type 5 waterborne epoxy system with the following materials:

- EFKA® 2526 (Ciba Specialty Chemicals, See Table 3)
- BYK® 024 (BYK-Chemie)
- BYK 033
- BYK 346
- DEE FO® PI-4 (Ultra Additives)
- Surfynol® DF-62 (Air Products)

Cure Catalysts

Cure catalysts are useful to decrease the time required to achieve a minimum hardness, and to achieve early water or solvent resistance. However, because they increase reactivity, they will also decrease pot life. Also, effective cure catalysts are usually tertiary amines. As such, using them will decrease acid and water resistance of the final formulation. A commonly used catalyst is 2,4,6-tris(dimethylamino)phenol (e.g., EPIKURE 3253).

Figure 6. Effect of Cure Catalyst on Hardness Development



Flash Rust Inhibitors

Flash rusting is a sporadic phenomenon that can occur during application of waterborne epoxy coatings to metallic substrates in high humidity conditions. It is especially problematic when the metal substrate is newly blasted steel. It can also be a problem when waterborne paints are applied on cool damp days because water release from the drying film is greatly slowed. It is believed that oxidation of ferrous to ferric ions on the metal substrate causes the distinctive rust spots of ferric hydroxide; a phenomenon known as flash rusting.

Several common flash rust inhibitors, such as lead naphthenate, tertiary amines, chromates, or dichromates should not be used because they are incompatible or ineffective. Nitrite salts (calcium or potassium salts are preferred) may be added to the epoxy and/or curing agent component. The following two commercial products give good results, but should be used in the curing agent component, as they cause instability of the epoxy component:

- RAYBO® 60 (Raybo Chemical Co. See Table 3.)
- Flash-X® 150 (Halox)

Because of the potential for poorer water and corrosion resistance, it is highly recommended that a thorough screen of each flash rust additive-modified formulation be conducted to ensure that an appropriate type and level has been utilized. Furthermore, the flash rust resistance of a specific formulation depends on the solids content of that coating. If an applicator reduces the viscosity of a waterborne coating simply by adding water, then there is a greater chance for flash rusting because the overall concentration of water in the coatings formula has increased. Increasing the amount of flash rust additive can compensate for this but check to ensure that the formulation retains sufficient water-resistance and corrosion-resistance for the given application.

Adhesion Promoters

Epoxy functional -, acrylate functional -, and amine functional - trialkoxy silanes have been used in solventborne and solventless epoxy coatings to improve substrate wetting and wet adhesion performance. In waterborne epoxy coatings, these materials give improved substrate wetting and adhesion, especially to galvanized steel, cold rolled steel, and aluminum. They are less effective on blasted or phosphated steel. In addition, they give faster cure and hardness development, as well as improved corrosion resistance.

The chemical structure of the additive is important. Epoxy-functional silanes, triethoxy silanes, or diethoxymethyl silanes give the best shelf stability. Amino silanes contribute to yellowing. Methoxy silanes hydrolyze to form homopolymers with poor adhesion.

Additives that give good performance in Type 5 waterborne epoxy coatings include:

- CoatOSil® 1770 (Hexion Performance Materials. See Table 3)
- Silquest® A2287 (Hexion Performance Materials)
- Dynasytan® GLYEO (Degussa)

Typical use levels for the epoxy silanes range from 0.5 to 3% weight of the epoxy resin dispersion. Higher use levels can cause orange peel in the coating, particularly, in low VOC primers. At the 1–3% weight use level, they provide improved hardness development, and early water and salt spray resistance. For example at 25°C and 55% R. H., the cure time for a waterborne white enamel to reach a 3B pencil hardness was reduced from 72 hours to only 30 hours by using 1.5% wt. CoatOSil 1770. Similarly, the cure time required for passing wet adhesion, after 60°C water immersion, was shortened from 14 days to only 10 days.

The best performance enhancements are obtained by incorporating the silane adhesion promoter into the epoxy component during the pigment grind. This results in smoother, glossier films with maximum cured film performance enhancements. Studies have shown that although epoxy functional “ethoxy” silane coupling agents seem to have acceptable water stability, one can premix the silane additive with other lipophilic modifiers to further enhance stability. The lipophilic additive (e.g., CARDURA E10P) seems to form a protective barrier as it carries the silane into the epoxy particle.

Mar and Slip Agents

These additives may improve abrasion resistance and early water resistance. Polydimethylsiloxanes or micronized polyethylene dispersions are useful in Type 1 or Type 2 waterborne epoxy coatings. The polyethylene dispersions may lower gloss. Aqueous wax dispersions are often used in Type 2 coatings. Silicones like BYK 307 are useful in this regard.

Fungicides and Mildewcides

Bacteria, molds, mildews and algae can attack waterborne paints (both wet and dry films). Bacteria attack latexes because they feed on the cellulosic thickeners and other colloids added to the latex formulation. To prevent such attack, latex formulators add fungicides to the formulation. To the best of our knowledge, fungicides are not required in waterborne epoxy formulations because they are not as susceptible to this type of problem. These additives can also cause stability problems. In regards to mildew growth on the dried coating, epoxy systems are more resistant to this type of attack because of their greater hardness and low “oil” content. For these reasons, fungicides and mildewcides are not generally used in waterborne epoxy formulations.

Thickening Agents and Thixotropes

Thickeners and thixotropes are used to maintain component stability by preventing settling, and for coating sag resistance. Component stability (12 months minimum), generally requires that the individual component viscosity should be greater than about 65 KU at 25°C. Many rheology control agents commonly used in latex coatings are unsuitable for thickening waterborne epoxy coatings because they contain, or are neutralized, with ammonia or other amines. These neutralizers will react with the epoxy groups, causing extreme viscosity build, gel formation, coagulation and pigment kick-out. The following materials can be used:

- Modified hydroxyethylcellulose (e.g., Natrosol® 250 MBR, Hercules-Aqualon)
- Fumed silicas (e.g., AEROSIL® R812, Degussa Corp.)
- Attapulgite clays (e.g., Attagel® 50, Elgelhard Corp.)
- Modified bentonite clays (e.g., Bentone® LT, Elementis Specialties)

HEUR thickeners work well to establish grind viscosity, and to stabilize the components. HEUR thickeners which work well in a Type 5 waterborne epoxy include OPTIFLO® H600 (Süd Chemie AG) and TAFIGEL® PUR-60 (Münzing Chemie GMBH).

Wetting or Dispersing Agents

Dispersing agents are generally required to coat the pigment and passivate the pigment’s oil demand. If this were not done, the pigment could absorb epoxy surfactants and/or cosolvents which would adversely affect dispersion stability and gloss. Anionic dispersants are often used in latex formulations. However, ionic dispersants should be avoided in waterborne epoxy systems, as they can cause gel formation, low gloss, reduced hardness, and poor water resistance. Non-ionic dispersants are strongly recommended for high-performance waterborne epoxies. Dispersants which work in a Type 5 waterborne epoxy include Lecithin (American Lecithin Company), and Anti-Terra® U (BYK Chemie). Especially good results have been achieved with 1:9 blends by weight of either OPTIFLO® HV600VF (Süd Chemie AG) and ETHOX TAM-20 (ETHOX Chemicals LLC), or OPTIFLO H600 and ETHOX TAM-20.

Dispersing Pigments

There are three ways to disperse pigments in waterborne epoxy coatings. The most preferred way is to disperse the pigments in the waterborne epoxy resin. This tends to give the best performance and stability. It is also possible to disperse the pigments in water and dispersant, and then let down the grind with the waterborne epoxy resin. However, this often requires the use of more dispersant which may adversely affect performance. Amine curing agents are usually good for wetting pigments, so pigment grinds can be done in the curing agent phase. Some waterborne amine curing agents may not give the best stability, so this must be checked carefully. It is also possible to disperse pigments in low molecular weight (low viscosity) polyamides. This grind can then be let down with the waterborne amine curing agent.

High-speed dispersers generally provide sufficient shear for preparing most primers and gloss enamels. The amount of water used in the grind phase should be minimized to minimize foam generation. Also, a defoamer may be used to suppress foam. Defoamer levels in the range of 2–4 pounds/100 gallons of paint are generally used (see example in Table 3). Additives such as surfactants, defoamers, and cosolvents should be blended into the waterborne epoxy resin before adding the pigments. Typical grind parameters include 2,000–2,500 rpm, 110–140°F, for 20–25 minutes.

Horizontal media mills such as sand mills can be used to prepare high gloss enamels and primers. Defoamer levels in the range of 4–6 pounds/100 gallons of paint are generally used. Additives such as surfactants, defoamers, and cosolvents should be blended into the waterborne epoxy resin before adding the pigments. The temperature should be maintained below 150°F.

Pebble mills or ball mills generally may also be used. A defoamer may be used to suppress foam. Defoamer levels in the range of 2–4 pounds/100 gallons of paint are generally used (See example in Table 3). Additives such as surfactants, defoamers, and cosolvents should be blended into the waterborne epoxy resin before adding the pigments. Typical grind parameters include 140–150° F, for 18–24 hours.

Pigment Selection

Important characteristics for pigments used in high-performance waterborne epoxy coatings include:

- Low oil and water absorption
- Low soluble salt content
- Low ionic character
- Extender pigments with various shapes and sizes used to improve packing
- Anti-corrosive pigments with acceptable water solubility, and pH greater than 6

Prime (Color) Pigments

Titanium Dioxide

Weatherable, surface-treated, easy-to-disperse grades of titanium dioxide are recommended for the best stability and performance. Grades like TI-PURE® R-960 (DuPont, see Table 3 for an example) and KRONOS® 2160 (Kronos, Inc.), or equivalent, are designed for maximum chalk resistance. These grades are typically 80–90% wt. TiO₂ with the remaining weight being a silica/alumina surface treatment. Other grades may yellow sooner. Lower cost buff grades of titanium dioxide may be used in primers. Typical loadings are in the range of 1.25–2.00 lb./gallon of paint.

Carbon Blacks

Neutral grades (e.g., pH = 6–8) should be used. Typical loadings are in the range of 0.01–0.05 lb./gallon of paint.

Red Iron Oxide

Synthetic red iron oxides are preferred for the best stability. Natural grades may contain soluble salts which will adversely affect stability. Easy to disperse grades with a neutral pH and a particle size of about 0.4–0.5 μm work well. RO-4097 Kroma Red® (Elementis Pigments Inc.), or equivalent generally work well. Typical loadings are 0.75–1.25 lb./gallon.

Yellow Iron Oxide

As with the red iron oxides, easy to disperse synthetic grades with neutral pH (e.g., 6–8) are preferred. Typical loadings are 0.75–1.25 lb./gallon.

Extender Pigments

Calcium meta-silicate is a useful extender and film reinforcement due to its acicular shape. Grades with surface treatment, such as 10ES Wollastocoat® (NYCO Minerals Inc.) or equivalent work well (see Table 3).

Barium sulfate (barytes) such as Sparmite A (Elementis Pigments Inc.) or equivalent contributes to water and chemical resistance (see Table 3).

Mica (aluminum potassium silicate) has a platy morphology that contributes to water and humidity resistance. 325 mesh water ground grades are preferred (see Table 3).

Silica-alumina ceramic microspheres have a low oil absorption and contribute to good pigment packing. They are useful in increasing filler loading and they enhance hardness and abrasion resistance. Grades that work well include Zeeospheres™ G-200 or G-400 (3M Specialty Materials) or equivalent.

Magnesium silicate (talc) is less preferred because it can lead to high viscosity. Low oil absorption grades like Lo Micron 399 may be useful in some formulations.

Calcium carbonate filler is generally not recommended, because high ionic content can adversely affect stability. Low oil absorption grades may be useful to reduce cost in some formulations. However, these formulations must be carefully evaluated for stability.

Aluminum silicate (china clay) is generally not recommended.

Anti-Corrosive Pigments

The key to finding an acceptable inhibitive pigment is to find one with a proper balance of solubility. Excessive solubility, or insolubility, will result in premature coating failure. Excessive solubility will show up as rapid loss of corrosion resistance after achieving good early performance. Insolubility will exhibit itself as poor early resistance that eventually levels off—if sufficient solubility is ultimately achieved. Avoid highly ionic species such as zinc phosphites, zinc borates and zinc phospho-oxide complexes.

Corrosion inhibiting pigments which have been successfully utilized are summarized in Table 9.

Table 9. Examples of Corrosion Inhibiting Pigments for Waterborne Epoxy Coatings

Pigment Type	Commercial Example	Manufacturer
Zinc modified aluminum triphosphate	K-White 105	Tayca
Strontium phosphosilicates	Halox® SW-111 (see Table 3)	Halox
Zinc phosphate complex	Halox Z-Plex 111	Halox
Calcium ion-exchange silica	Shieldex	W.R. Grace
Zinc silicate modified aluminum triphosphate	K-White 84	Tayca
Modified aluminum triphosphate	K-White 108	Tayca
Zinc phosphate complex	J-0852	Rockwood Pigments
Calcium phospho silicates	Halox CW-491	Halox
Aluminum zinc phosphate hydrate	Heucophos® ZPA	Heubach GmbH
Calcium phosphate	Halox 430	Halox

Halox has evaluated corrosion inhibitors in Type 5 waterborne epoxy coatings. Figures 7a and 7b (see inside of back cover) were provided by Halox and display key results from these evaluations. Excellent results are noted in both figures with calcium phosphate (Halox 430). Even better results were found when using a combination of calcium phosphate (Halox 430) and a proprietary organic corrosion inhibitor (Halox 520).

Primer Pigmentation

The PVC should be in the range of 30–45%. Optimums are usually found in the range of 35–40%. Lower PVC levels generally result in lower application solids, early blistering at high humidity, and greater tendency to flash rusting. Table 10 summarizes typical pigment levels.

Table 10. Typical Primer Pigmentation Levels

Pigment Type	% Volume
Anti-corrosion pigment	5.4–8.5
Color pigment (e.g., red iron oxide)	4.9
Extended pigments	
calcium metasilicate	12.5
silica-alumina ceramic microspheres	10.1
barium sulfate	1.2–4.4
mica	0.9
Total	~38

Type 5 Waterborne Epoxy Formulations

Using the principals previously summarized, the Type 5 waterborne epoxy was used to formulate a white enamel, a white primer, and a red iron oxide primer. These formulations are summarized in Table 11. The performance of these coatings is summarized in Table 12.

The performance of the waterborne enamel is compared to that of a conventional solvent based epoxy enamel. The performance of the waterborne coating is equivalent to that of the solvent based coating, with the exception that the waterborne coating gives low VOC (1.53 lb./gal.), more rapid dry, and superior corrosion resistance in the salt spray test. The waterborne primers give fast dry and excellent corrosion resistance.

Table 11. Waterborne Epoxy Starting Point Formulations						
Material	White Enamel		White Primer		Red Primer	
Part A	Pounds	Gallons	Pounds	Gallons	Pounds	Gallons
Epoxy resin dispersion (e.g., EPI-REZ 6520) ¹	387.3	43.02	300.0	33.33	300.2	33.35
Dipropylene glycol n-butyl ether (DPnB) ²	20.6	2.72	—	—	28.2	3.72
Propylene glycol phenyl ether (PPh) ²	26.0	2.95	30.6	3.47		
Propylene glycol methyl ether (PM) ³	—	—	—	—		
Glycidyl ether of neodecanoic acid (e.g., CARDURA® E-10P) ¹	10.8	1.35	—	—		
Surfactant (e.g., TAM-20)	4.5	0.82				
Defoaming agent (e.g., EFKA 2526) ⁵			3.0	0.35		
Defoaming agent (e.g., EFKA 27) ⁵					2.8	3.7
Defoaming agent (BYK 22) ⁵	0.4	0.05				
Rutile titanium dioxide (e.g., TI-PURE® R-960) ⁶	198.2	6.14	100.0	3.10		
Red iron oxide (e.g., KROMA® RO-4097) ⁷			—	—	62.8	1.54
Calcium metasilicate (epoxy-silane treated) ⁸ (e.g., 10ES WOLLASTOCOAT®)			100.0	4.12	93.8	3.87
Barium sulfate (e.g., SPARMITE®) ⁷			67.0	1.83	62.8	1.71
Anti-corrosive pigment (e.g., HALOX® SW-111) ⁹			94.7	3.98	87.8	3.51
Ceramic silica-alumina alloy (e.g., ZEOSPHERES® 400) ¹⁰			—	—	62.6	3.12
Muscovite mica (e.g., WG mica – 325 mesh) ¹¹			7.0	0.30	6.6	0.28
<i>High Speed Disperse to texture of</i>			<i>5–6 Hegman</i>		<i>5–6 Hegman</i>	
Epoxy resin dispersion (EPI-REZ 6520) ¹			147.8	16.42	93.1	10.35
Thickening agent (e.g., OPTIFLO® H600) ¹²	0.4	0.05	—	—		
Adhesion promoter (e.g., CoatOSil 1770 silane) ¹³			8.6	0.98		
Defoamer (Drew Plus L-475)	1.0	0.13				
Water	190.1	22.77	101.2	12.12	110.0	13.18
Total Part A	839.3	80.00	959.9	80.00	910.7	75.00
Part B						
Amine curing agent dispersion ¹ (e.g., EPIKURE 6870)	172.4	18.95	180.0	19.78	180.0	19.95
Epikure 3253	5.0	0.61				
Water					42.2	5.05
Flash rust additive (e.g., RAYBO® 60) ¹⁴	0.8	0.09	2.0	0.22		
Texanol	2.8	0.36				
Total Part B	181.0	20.00	182.6	20.00	222.2	25.00

Typical Properties			
Solids content (%wt. / % vol.)	50.2% / 40.8%	62.7% / 48.9%	60.1% / 45.2%
PVC, %wt.	15	27.2	31.1
VOC	1.38 lb./gal. 165 g/l	0.82 lb./gal. 98 g/l	0.69 lb./gal. 83 g/l
Pot life, hr.	3–4	4–5	3–4

¹Hexion Specialty Chemicals

²Dow Chemical Co.

³Shell Chemical Co.

⁴Byk-Chemie

⁵Lubrizol

⁶DuPont

⁷Elementis Pigments

⁸Nyco Minerals

⁹Halox Pigments

¹⁰Zeeland Industries

¹¹Franklin Ind. Minerals

¹²Sud-Chemie

¹³Witco Company

¹⁴Raybo Chemicals

Table 12. Performance of Waterborne Epoxy Starting Formulations				
Property	White Enamel ¹	Solventborne Enamel ²	White Primer ³	Red Primer ⁴
Dry times				
Tack-free, hr.	4.75	3.5	0.5	0.25
Thru-dry, hr.	7.5	8.5	1.5	7.5
Pencil hardness (24 hr. / 14 days)	3B-2B/F	4B/H	F/F	2B/F
Gloss values (60° / 20°)	99/84	95/87	25/4	
Impact resistance (dir./rev.), in.-lb.	160/160	160/160	28/4	16/2
MEK double rubs	160	337	150	
DI water immersion (25°C), days	>500	>250	>83	
ASTM blister rating, field	8M, 6M	10 (none)	10 (none)	#8 Med
Salt spray resistance, hr.	>500	1152	>750	1152
ASTM blister rating, field	6M	6F-6M	10	#6 VF

¹ WB White enamel (e.g., Starting Formulation 1705 – Hexion Specialty Chemicals)

² Epoxy polyamide binder (e.g., EPON Resin 1001 / EPI-CURE 3115 Curing Agent – Hexion Specialty Chemicals)

³ WB White primer (e.g., Starting Formulation 1700 – Hexion Specialty Chemicals)

⁴ WB Red primer (e.g., Starting Formulation 1729 – Hexion Specialty Chemicals)

Formulation Tips

End of Pot Life

A visible end of pot life, in terms of a significant viscosity increase or gelation, is preferred, as it signals the painter that painting with this particular mix should be discontinued, and a new mix should be made to continue painting. Formulation factors which must be considered include:

- Decreasing PVC (increasing resin content) favors viscosity increase and gelation prior to end of pot life.
- The solids content of the paint should generally be above 52% by weight.
- Increasing the amount of hydrophobic diluent will enhance visible end of pot life.
- Adding 5% of a liquid epoxy resin (e.g., EPON 828) is more effective than adding 5% of a reactive diluent like the glycidyl ester of neodecanoic acid (e.g., CARDURA E10P) to the epoxy dispersion.
- Increase the amount of “tail solvent,” MnAK or DPnB.
- Switch to EP or DPM as the sole cosolvent in the formulation.
- Evaluate a 1:1 (by weight) blend of DAA/PnB as the cosolvent.
- Increase the amount of curing agent (relative to epoxy) in the formulation by about 5%.

Improved Corrosion Protection

- Decrease the PVC to increase the barrier properties of the film.
- Optimize corrosion inhibitive fillers and pigments.
- Fully cure the films before testing in corrosive environments.
- Increase the ratio of epoxy to amine by 5–10%.
- Use commercial flash rust inhibitors, rather than inorganic nitrite solutions.
- Use epoxy-functional ethoxysilane additives to improve substrate wetting, adhesion, and surface hydrophobicity.

Component Stability

- Use only non-ionic surfactants, wetting aids, and thixotropes.
- Minimize the use of primary alcohols, or primary hydroxyl glycol ethers as cosolvents in the epoxy component.
- Avoid excessive grind temperatures during pigment dispersion.
- Use a 1:1 by weight blend of either DAA/PnB or DAA/MnAK as the cosolvent to minimize viscosity increase during storage of the epoxy component.

Faster Cure and Hardness

- Replace slow cosolvents (e.g., PPnB) with PPh or PM.
- Modify the epoxy with 10–3-% by weight of an epoxy novolac dispersion (e.g., EPI-REZ 5003-W-55). This also improves chemical resistance.
- Modify the epoxy component with a high molecular weight epoxy dispersion (e.g., EPI-REZ 354e5-WY-55).
- Additional of Isopropanol.

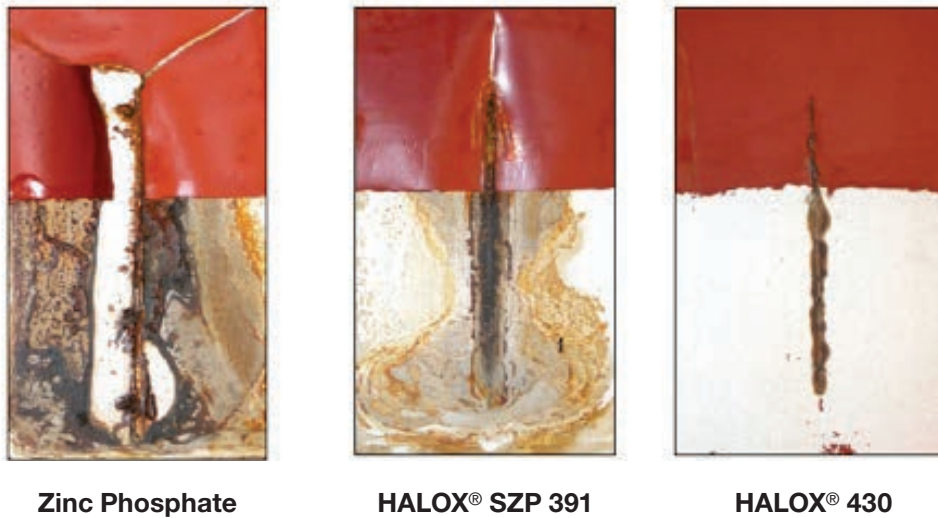
Things to Avoid

- Highly water soluble tail solvents
- All borate based inhibitive pigments that cause package instability
- Anionic additives (wetting aids, dispersants, thickeners, etc.), especially those neutralized with amines or alkali
- Additives or modifiers with amine functional groups or neutralized amines
- “Slurry” grades of TiO₂ (use automotive grades for best performance)
- Oxidized carbon black grades with low pH; use grades with pH = 6–8
- Pigments and fillers with oil absorption ≥30
- Methoxy-based silanes for wet adhesion
- Aqueous acrylic additives or colorants

Conclusions

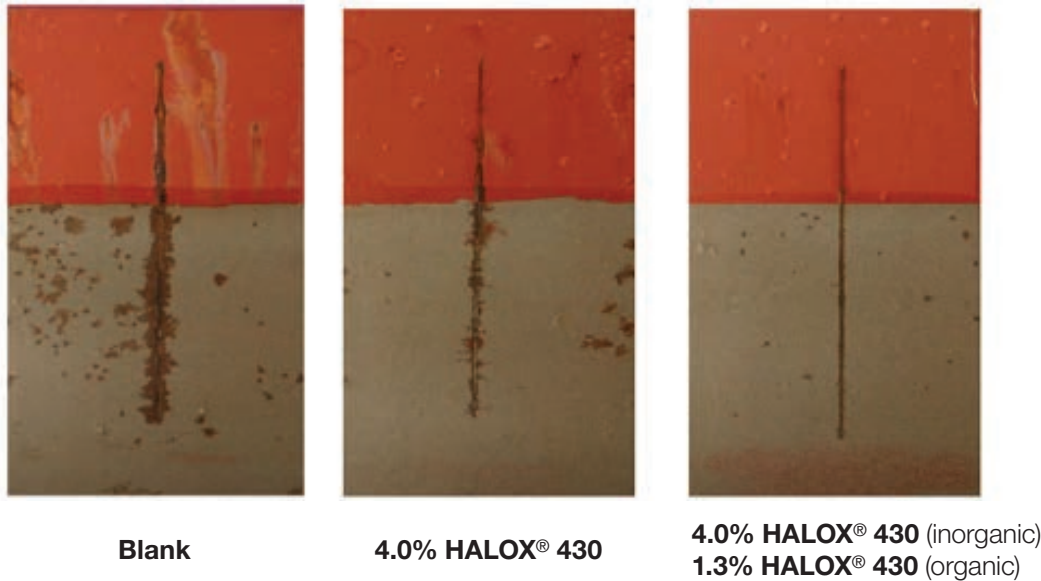
Using the most recent waterborne epoxy technology, high-performance waterborne epoxy coatings can be formulated which match or exceed the performance of solvent-based coatings at attractively low VOC. In order to achieve high levels of performance, the components and additives used must be carefully studied and selected. Formulating techniques which are specific to waterborne epoxy technology must be employed.

Figure 7a. Corrosion Inhibitors in Type 5 Waterborne Epoxy



Substrate is cold rolled steel. Dry film is 2–3 mils. Loading is 4% TFW. Salt spray: 336 hours ASTM B-117.

Figure 7b. Corrosion Inhibitors in Type 5 Waterborne Epoxy



Substrate is blasted hot rolled steel. Dry films are 3.0–3.5 mils. Loading: 4% TFW. Salt spray: 500 hours ASTM B-117. Data and pictures were kindly provided by Halox.

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