



NEW W EPOXY RESIN DISPERSION

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Unfortunately, existing waterborne 2K epoxy primers are generally regarded as inferior in terms of corrosion and humidity resistance, when compared to their solventborne counterparts. In addition, it is believed that many waterborne systems require the use of inorganic corrosion-inhibitive pigments, such as zinc phosphates, in order to provide adequate corrosion protection. The possible drawbacks of using anticorrosion pigments include higher formulation cost, difficulties in pigment dispersion, poor formula stability, and potential environmental concerns. For example, primers containing between 2.5%–25% of zinc phosphate are classified as environmentally hazardous in Europe in accordance with Preparation Directive 1999/45/EC.

It is found that a novel, internally emulsified and flexibilized waterborne epoxy resin dispersion, Epoxy 386, can be used to formulate low-VOC (~100 g/L and less) 2K primers which are free of corrosion-inhibitive pigments, but with anticorrosion performance comparable to a commercially available solventborne 2K epoxy system.

Furthermore, this epoxy resin is shear stable, which enables formulators the flexibility of grinding pigments, such as titanium dioxide and barium sulfate, directly in the epoxy portion using high-shear dispersers or bead mills. Since the hardener resin generally represents the smaller component, direct grinding inside the epoxy portion means more liquid binder volume is available for processing. This leads to other formulation possibilities including improved ease of manufacturing and higher pigment-to-binder (P/B) ratio for cost reduction.

Moreover, the flexibility of this epoxy resin provides an added benefit of enhancing the adhesive properties of a coating. It was previously shown¹ that while the flexibilities of both waterborne and solventborne epoxy primers could decline upon aging for seven days at elevated temperature (50°C), only waterborne primers based on Epoxy 386 maintained adequate flexibility after aging compared to two other primers based on non-flexibilized epoxy resins. In addition, they outperformed another commercially available waterborne 2K epoxy system.

Table 1—Formulations evaluated in this study

	Formula 1	Formula 2	Formula 3
Calculated VOC	102 g/L	92 g/L	80 g/L
Part A			
Epoxy 386	46.20	46.20	46.20
Dispersant 6208/60	1.30	—	—
Dispersant 6208 (low-VOC version of 6208/60)	—	1.56	1.56
Defoamer	0.30	0.30	0.30
De-ionized Water	9.15	8.89	8.89
Talc	5.60	5.60	5.60
Titanium dioxide	19.70	19.70	19.70
Yellow iron oxide	0.25	0.25	0.25
Black iron oxide	0.80	0.80	0.80
Barium sulfate	15.40	15.40	15.40
<i>Bead mill grind to minimum Hegman 5 then slowly add:</i>			
High-boiling ester-alcohol solvent (EA)	0.60	0.60	—
Associative thickener	0.70	0.70	0.70
Part B			
Hardener 2188	13.20	13.20	13.20
Water	1.80	1.80	1.80
Total: Parts A+B	115.00	115.00	114.40
Stoichiometry HEW:EEW ~ 0.75:1.0 P/B ratio ~ 1.28:1			

EXPERIMENTAL

Materials and Formulations

Two commercially available 2K epoxy-amine anticorrosion primers were obtained in the U.S. for this study. The first primer, WB-X, was a waterborne coating with VOC reported at <250 g/L. The second primer, SB-Y, was a solventborne semi-gloss system with VOC reported at <300 g/L after solvent reduction as suggested by its manufacturer.

Three slightly different test formulations, with calculated VOC levels of 102 g/L, 92 g/L, and 80 g/L, were evaluated in this study (Table 1). Pigments were ground directly in the epoxy portion.

Characteristics of waterborne epoxy resin and hardener used in these formulas:

(1) Epoxy 386: A 52% active epoxy resin dispersion with epoxy equivalent weight (EEW) at ~1,000 g/mol as supplied. Viscosity ranges from 300–1,500 mPa.s.

(2) Hardener 2188: A 55% active, hydrophobically modified aliphatic amine hardener with H-equivalent weight (HEW) at ~380 g/mol as supplied. Viscosity ranges from 6,000–14,000 mPa.s. This hardener is commercially available for 2K waterborne anticorrosion primers, and it was found to work well together with Epoxy 386.

A stoichiometry ratio HEW:EEW of 0.75:1.00 was chosen since this ratio was previously determined to provide a very good balance in corrosion (salt spray) and humidity resistance.²

The difference in calculated VOC among these formulas is due to (a) the usage of different

delivery forms of a polymeric type pigment dispersant (6208/60 is supplied in a blend of organic solvents, while 6208 is supplied in mostly water and contains only 1% of organic solvent); and (b) the usage of a high-boiling ester-alcohol solvent, EA. It is believed that at least some EA remained in the coating films even after curing at room temperature for more than 10 days. However, we took a conservative approach in our VOC calculation and treated EA as 100% volatile for this study.

Preparation of Primers and Coated Panels

Commercial primers WB-X and SB-Y were prepared according to their respective manufacturers' recommendations before application. Both systems required an induction period of 30 min after mixing Parts A and B (activation), and were applied to panels shortly after the induction was finished. Formulation details such as stoichiometry and P/B ratio of either primer are unknown.

Test Formulas 1, 2, and 3 were prepared by mixing Parts A and B together, with an additional 6% of water to lower viscosity for ease of spraying. An induction period of 30 min was allowed before application. All test panels were coated shortly after the induction was finished, except those prepared specifically for pot life study.

All metal panels were coated by conventional pressure-feed air spray. Three types of metal panels were used in salt spray and crosshatch adhesion tests: sand-blasted steel (SB, Custom Lab Specialties brand, 11 gauge cold rolled), cold-rolled steel (CRS, Q-Panel brand Type S, ground finish), and aluminum (AL, Q-Panel brand Type A, bare mill finish). All other tests were performed on CRS panels only. All test panels were single coated. Dry film thickness (DFT) on these panels was targeted as shown in *Table 2*. A slightly higher film thickness of SB-Y was targeted on CRS and AL panels based on recommendation from SB-Y's manufacturer.

All coated panels were dried and cured at room temperatures (72 ± 2)°F for 10 days before subjected to corrosion-related testing, including salt spray (fog), humidity resistance, and water-immersion tests. All other testing was done after the primers were allowed to dry and cure at room temperatures for seven days.

Table 2—Targeted DFT of primers on different metal substrates

Dry Film Thickness (mils)	Test Formulas		
	1, 2, and 3	WB-X	SB-Y
SB	3–5	3–5	3–5
CRS	2–3	2–3	3–4
AL	2–3	2–3	3–4

Performance Testing

Corrosion Testing

Salt spray testing was done according to ASTM B 117-03. Coated panels were scribed according to ASTM D 1654-05 before exposure. Ratings for maximum creepage at scribes were given according to the same method. A rating of “10” represents zero creepage, while a rating of “0” represents a maximum creepage of >16 mm.

Humidity resistance testing was done according to ASTM D 4585-99 using a Cleveland condensing type humidity cabinet with temperature set at (38–40)°C.

Water-immersion testing was done by immersing the coated panels in de-ionized (DI) water with temperature maintained at (40–42)°C. At each evaluation interval, panels were removed from the water, wiped dry, rated immediately, and then returned back to water immersion.

For all three corrosion tests mentioned above:

(a) Panel appearance was evaluated and the degree of blistering was rated according to ASTM D 714-02. A blister size rating of “10” represents no blistering, while a size rating of “2” represents large blisters. Frequency of blisters was also rated according to ASTM D 714-02, with “F” = few, “M” = medium, “MD” = medium dense, and “D” = dense.

(b) Degree of surface rusting was rated according to ASTM D 610-01. A “10” rating represents $\leq 0.01\%$ of surface rusted, while a “0” rating represents >50% surface rusted. Rust distribution type was described as either “S” (spot rusting), “G” (general rusting), “P” (pinpoint rusting), or “H” (hybrid rusting).

Other Testing

Crosshatch adhesion was performed according to ASTM 3359-07, with 2 mm spacing between cuts. 3M's Scotch brand tape type 898 was used. A rating of “5B” represents 0% of coating was detached, while “0B” represents >65% of coating was detached. For adhesion ratings less than 5B, numbers in parenthesis following the adhesion rating represent the estimated percentage of coated area with coating detached.

Pencil hardness was checked on CRS panels per our internal method, SOP ST-LC-26, which is similar to ASTM D 3363-05.

Using a handheld gloss meter on CRS panels, 60° gloss was measured according to our internal method, SOP ST-LC-28, which is similar to ASTM D 523-89.

Chemical resistance was evaluated using 24-hr spot test. Testing was performed on CRS panels according to our internal method, SOP ST-LC-46, which

Table 3—Salt spray exposure results

Time Exposed: Appearance Sample	168 hr				504 hr				1,008 hr			
	Blister	Rust	Scribe	Blisters at the Scribe	Blister	Rust	Scribe	Blisters at the Scribe	Blister	Rust	Scribe	Blisters at the Scribe
Formula 1												
SB	10	10	9	6M	10	10	9	6M	10	10	8	6M
CRS	10	10	7	6M	10	10	6	6M	10	10	5	4-6 M-MD
AL	10	10	10	10	10	10	10	10	10	10	10	10
Formula 2												
SB	10	10	9	6-8F	10	10	9	6M	10	10	8	6M
CRS	10	10	8	6F	10	10	5	4-6 F-M	8F	10	5	4-6 M-MD
AL	10	10	10	10	10	10	10	10	10	10	10	8F - 10
Formula 3												
SB	10	10	9	8F	10	10	9	6F	10	10	8	6 F-M
CRS	10	10	8	6F	10	10	9	6F	8F	10	6	4-6 M
AL	10	10	10	10	10	10	10	10	10	10	10	10
WB-X												
SB	6F	8G-9S	9	6-8F	4-6 F-M	7-8 G	9	4-6 F-M	4-6 MD-D	5-6G	8	4-6 MD
CRS	6F	8P-9G	2	6F	4-6M	7P-8G	0	6 MD-D	4-6 M	6P-7G	0	4-6 D
AL	10	10	10	10	10	10	10	10	10	10	10	10
SB-Y												
SB	10	10	9	6-8F	10	10	9	4-6 F-M	8F-10	8G-10	9	4-8 MD
CRS	10	10	9	4-6 M-MD	10	10	7	4-6 M-MD	10	10	3	4M
AL	10	9S-10	10	6-8F	10	9S-10	10	6-8F	10	9S-10	10	8F

is similar to ASTM D 1308-02. Spots were evaluated immediately after reagents were removed.

MEK resistance (double rub) was checked on CRS panels per our internal method, SOP ST-LC-23, which is similar to ASTM D 5402-93.

RESULTS AND DISCUSSIONS

Corrosion Testing

Evaluation results of scribed panels after 168 hr (1 week), 504 hr (3 weeks), and 1,008 hr (6 weeks) of salt spray exposure are summarized in Table 3.

Formula 1 Compared to WB-X and SB-Y

It was found that Epoxy 386-based Formula 1 performed slightly better than SB-Y after 1,008 hr of exposure, even though SB-Y had a small advantage of slightly higher dry film thickness on CRS and AL panels. The creepage of Formula 1 on CRS was better than that of SB-Y after 1,008 hr (Figure 1). In addition, while both AL and SB panels of Formula 1 showed no blistering or rusting, an AL and a SB panel of SB-Y showed small signs of corrosion at the unscribed area.

On the other hand, even though Formula 1 is more or less equal in corrosion protection to WB-X on AL panels, Formula 1 outperformed WB-X significantly on both SB and CRS panels. WB-X started showing face rust and blisters after only 168 hr of exposure, while Formula 1 remained free of rust or blisters at the unscribed area even after 1,008 hr of exposure. Moreover, creepage rating of WB-X on CRS was much worse than that of Formula 1 (Figure 1).



Figure 1—CRS panels of Formula 1, WB-X, and SB-Y after 1,008 hr of salt spray exposure.

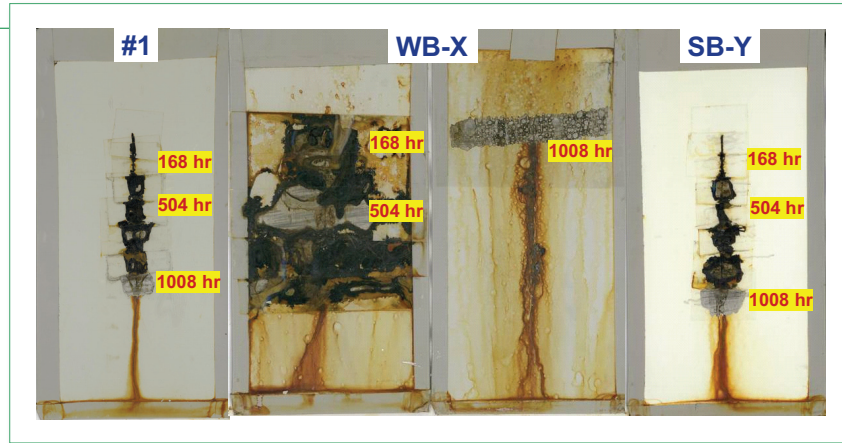
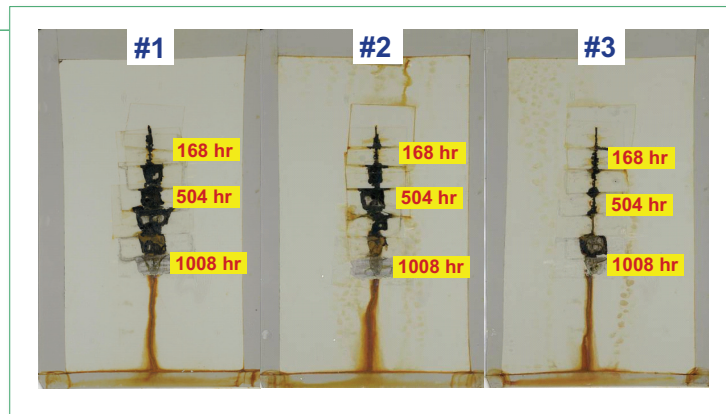


Figure 2—CRS panels of Formulas 1, 2, and 3 after 1,008 hr of salt spray exposure.



Comparing Formulas 1, 2, and 3

In general, Formulas 1 and 2 performed quite similarly on all three types of metal panels. This indicates the slight reduction in overall formula VOC (by substituting the polymeric dispersant from its high-VOC to low-VOC version) had no significant negative impact in salt fog resistance. Furthermore, coated CRS panels of both Formulas 1 and 2 have similar gloss levels after activation (*Figure 5*). This suggested that the small amount of solvents coming from the dispersant did not make a difference in the film formation and, therefore, probably did not have any impact in the barrier property of either primer.

On the other hand, CRS panels of Formula 3 performed somewhat better than those of both 1 and 2 in salt spray resistance (*Figure 2*). This is contradictory to what was originally expected: that the addition of a high-boiling solvent EA in a low-VOC waterborne formula would enhance film formation and therefore improve the resulting barrier property against corrosion.

It was thought that at least some EA solvent molecules remained in the primer films of Formulas 1 and 2 even after curing at room temperature for 10 days. If this indeed the case, these EA molecules might become the “weak links”

within those films, resulting in poorer barrier properties of Formulas 1 and 2. In addition, since all three Epoxy 386-based formulas performed similarly in humidity resistance and water-immersion tests (see results shown in *Tables 4 and 5*), these “weak links” created by leftover EA molecules *might* be especially sensitive to the presence of salt used in salt fog. Additional work is needed in order to investigate this further.

Humidity resistance results, after exposure periods of 168, 504, and 1,008 hr, are summarized in *Table 4*.

Formula 1 performed very similarly to SB-Y up to 504 hr of exposure. However, it showed a few small blisters after 1,008 hr and was therefore slightly worse than SB-Y, which remained free of blisters. In contrast, WB-X showed signs of blistering at 504 hr and got worse (in terms of size and frequency of blisters) after 1,008 hr of exposure (*Figure 3*).

On the other hand, Formulas 1, 2, and 3 performed very similarly after exposure to condensing water, indicating the formula differences among them had no visible effect on performance.

Water immersion test results, after 168, 504, and 1,008 hr of immersion, are summarized in *Table 5*.

Results from the water immersion test showed a similar trend to that of the humidity resistance test—formulas based on Epoxy 386 performed very comparably to SB-Y, and in turn both systems performed significantly better than WB-X (Figure 4). Note that WB-X showed more severe blistering after water immersion than exposure in a Cleveland-type humidity cabinet.

Other Testing

Results of other tests are summarized in Table 6. All Epoxy 386-based primers showed very good adhesion to all three types of metal panels (no more than 1% of coating loss) and they were comparable to both WB-X and SB-Y. SB-Y showed a slightly inferior adhesion on SB panels.

After seven days of curing at room temperature, the pencil hardness of all Epoxy 386-based primers was slightly lower than that of their waterborne counterpart WB-X, which in turn was softer than SB-Y. The relative softness of primers based on Formulas 1, 2, and 3 was somewhat expected since Epoxy 386 is internally flexibilized by design. Conversely, after conditioning at room temperature for two months, all primers became harder. The pencil hardness of Formulas 1 through 3 was about equal to that of WB-X, and SB-Y remained the hardest.

In this study, pencil hardness of different primers did not show any direct correlation to their corresponding anticorrosion performance. Additionally, test data reported here confirms that the chemical modification utilized to make Epoxy 386 flexible did not seem to impart any negative influence on corrosion resistance.

MEK double-rub and 24-hr spot-test results indicated Epoxy 386-based primers have better resistance to sulfuric acid and sodium hydroxide solutions, equal resistance to MEK, but slightly poorer resistance to xylene, when compared to WB-X. In contrast, SB-Y has better resistance to sulfuric acid, sodium hydroxide, and MEK, but poorer resistance to xylene, when compared to Epoxy 386-based primers.

Overall, primers made with Epoxy 386 have chemical resistance ranked somewhere in between WB-X and SB-Y. This might still be acceptable in applications where (a) the primers are protected by their topcoats; or (b) the primers are not expected to be exposed to harsh chemicals for an extended period of time. Additionally, chemical resistance of Formulas 1–3 might be further improved by adjusting the stoichiometry ratio and other formulation parameters.

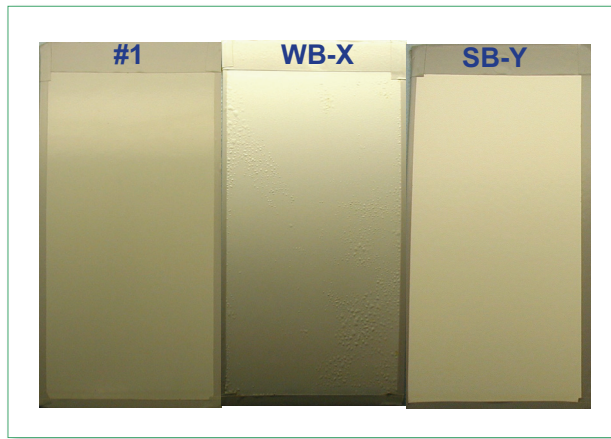


Figure 3—CRS panels after 1,008 hr of exposure in Cleveland-type humidity cabinet.



Figure 4—CRS panels after 1,008 hr of immersion in DI water.

Table 4—Humidity resistance test results

Time Exposed: Appearance	168 Hr		504 Hr		1,008 Hr	
	Blister	Rust	Blister	Rust	Blister	Rust
Sample						
Formula #1	10	10	10	10	8F	10
Formula #2	10	10	10	10	8F	10
Formula #3	10	10	10	10	8F	10
WB-X	10	10	8F - 6-8M (Clusters)	10	6-8M (Clusters)	10
SB-Y	10	10	10	10	10	10

Table 5—Water immersion test results

Time Exposed: Appearance	168 hr		504 hr		1,008 hr	
	Blister	Rust	Blister	Rust	Blister	Rust
Sample						
Formula 1	10	10	10	10	8F-10	10
Formula 2	10	10	10	10	8F-10	10
Formula 3	10	10	10	10	8F-10	10
WB-X	6-8 MD	10	6-8 MD	10	4-6 D	9P-8G
SB-Y	10	10	10	10	10	10

Table 6—Summary of adhesion, hardness, chemical spot, and MEK resistance test

	#1	#2	#3	WB-X	SB-Y
Crosshatch Adhesion (5B = best)					
SB	4B (1%)	4B (1%)	5B (0%)	4B (1%)	3B (6%)
CRS	4B (1%)	4B (1%)	4B (1%)	5B (0%)	4B (3%)
AL	4B (1%)	4B (1%)	4B (1%)	5B (0%)	4B (2%)
Pencil Hardness					
7 days	4B-3B	4B-3B	4B-3B	3B-2B	HB-F
2 months	HB-F	HB-F	HB-F	HB-F	H-2H
24-hr Spot Tests					
Water	Very slight loss of gloss	Very slight loss of gloss	Very slight loss of gloss	Very slight loss of gloss	Very slight loss of gloss
10% Sulfuric acid	Discoloration—yellowing slight softening	Discoloration—yellowing slight softening	Discoloration—yellowing slight softening	Bubbled and peeled off	Slight discoloration—yellowing
Gasoline	Slight loss of gloss	Slight loss of gloss	Slight loss of gloss	Slight loss of gloss	Slight loss of gloss
Motor oil 5W-30	OK	OK	OK	OK	OK
Xylene	Slight softening	Slight softening	Slight softening	Slight loss of gloss	Blistering
10% sodium Hydroxide	Slight loss of gloss and softening	Slight loss of gloss and softening	Slight loss of gloss and softening	Blistering, slight softening	Very slight discoloration
MEK Double Rubs					
Double rubs to cause >50% coating loss	40-50	40-50	40-50	40-50	90-100

Lastly, we checked the pot life of Formulas 1 and 2 by monitoring their gloss (*Figure 5*) and salt spray resistance on CRS panels at different time intervals after activation.

Even though 60° gloss profiles of both Formulas 1 and 2 indicated that their end of pot life is approximately 3 hr after activation, salt spray test results showed only a slight drop-off in corrosion resistance even when these two primers were applied 5 hr after activation. Additional tests, including humidity resistance and water immersion, are needed to confirm if overall properties at 5 hr after activation are indeed acceptable. Moreover, future work includes the pot life evaluation of Formula 3.

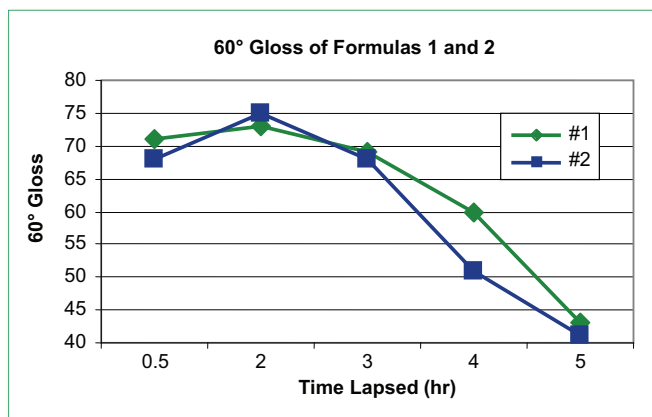


Figure 5—Gloss levels at different time intervals after mixing Parts A and B.

CONCLUSIONS


By utilizing the novel epoxy resin evaluated in this study, together with the correct selection of a matching hardener as well as the employment of proper formulation techniques, it is found that formulating high-performance waterborne 2K epoxy-amine primers with properties equal to or better than commercially available primers is quite possible. At the same time, the following requirements can be fulfilled:

- Low VOC (<100 g/L)
- Free of anticorrosion pigments, including zinc phosphate
- Excellent corrosion resistance
- Very good adhesion
- Pot life of 3 hr or more
- More formulation flexibility in terms of pigment grinding

FUTURE WORK

Additional R&D work is ongoing since there are still a few questions to be answered. For example, it was previously found that Epoxy 386-based primers containing no corrosion-inhibitive pigments actually had better salt fog resistance than similar primers containing zinc phosphate or other anticorrosion pigments.^{1,2} This seems contradictory to conventional wisdom. There might be drawbacks to using these active pigments, which are more than enough to negate any benefits provided by them.

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