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 hydraate	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
High Speed Disperse to texture of			*5–6 Hegman*		*5–6 Hegman*	
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

[1]Momentive Specialty Chemicals [2]Dow Chemical Co. [3]Shell Chemical Co. [4]Byk-Chemie
[5]Lubrizol [6]DuPont [7]Elementis Pigments [8]Nyco Minerals [9]Halox Pigments
[10]Zeeland Industries [11]Franklin Ind. Minerals [12]Sud-Chemie [13]Witco Company [14]Raybo 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 – Momentive Specialty Chemicals)

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

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

[4] WB Red primer (e.g., Starting Formulation 1729 – Momentive 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.

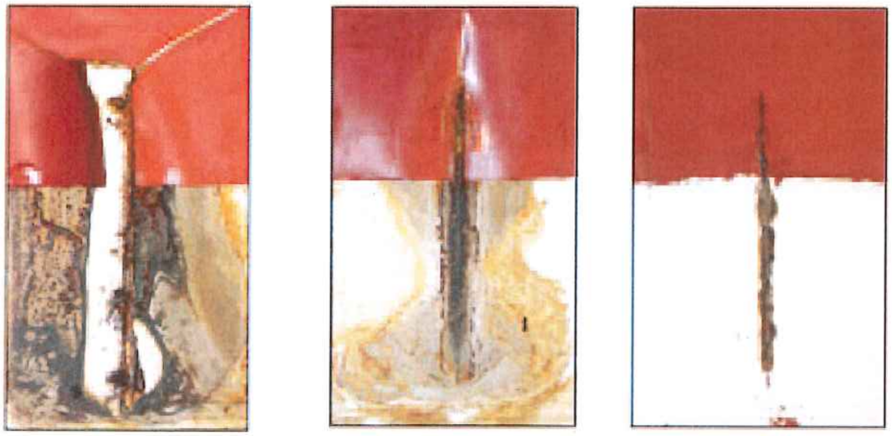
Things to Avoid

- 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 TiO_2 (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.

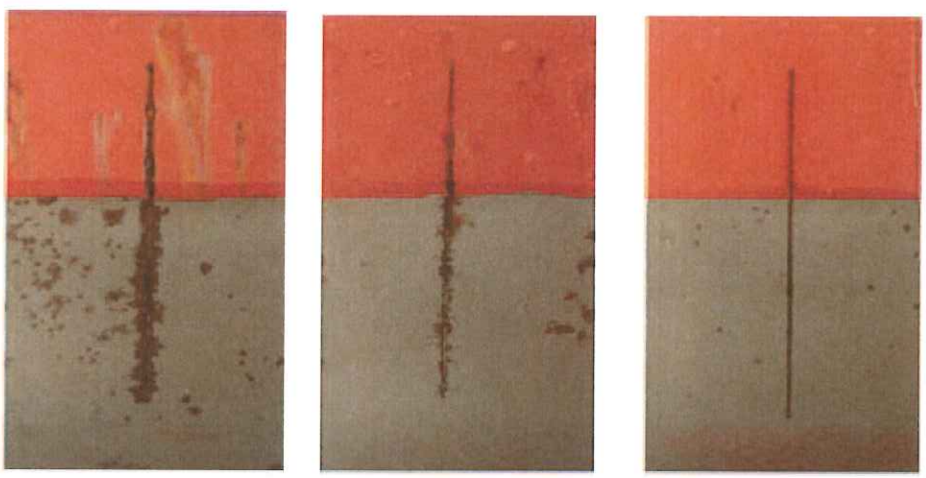
Figure 7a. Corrosion Inhibitors in Type 5 Waterborne Epoxy



Zinc Phosphate	HALOX® SZP 391	HALOX® 430

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



Blank	4.0% HALOX® 430	**4.0% HALOX® 430** (inorganic) **1.3% HALOX® 430** (organic)

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.