

Novel CNSL-based Waterborne



Zn-rich Primer Systems for Protective Coatings

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Low-VOC waterborne (WB) Zn-rich primers and high performance WB epoxy primers have been developed based on novel Cashew Nutshell Liquid (CNSL)-derived curing agents for industrial and protective coating applications. These unique WB phenalkamines were synthesized from a natural, non-food chain and renewable biomaterial and could help formulate WB primer systems that meet stricter volatile organic compound (VOC) regulations as well as high performance requirements.

This article presents the latest performance studies of new phenalkamine-based WB Zn-rich primers and epoxy primers, and discusses the challenges associated with such formulations.

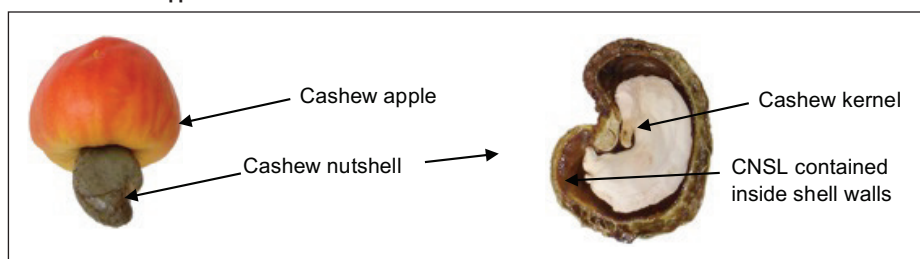
New 2K WB Zn-rich primers were formulated with a water-free phenalkamine curing agent. The study results showed the WB Zn-rich primers had good compatibility with various commercially available solid epoxy dispersions and delivered good cure and mechanical properties; importantly, those WB Zn-rich primers provided superb adhesion to both metal substrates and commercial polyurethane (PU) topcoats without the use of adhesion promoters. Excellent corrosion protection and good resistance to undercutting at the scribe were observed after 3000-h Q-Fog exposure.

Additionally, newly developed WB high performance primers based on zero-VOC WB phenalkamines were evaluated either in combination with WB Zn-rich primers or by being directly applied over metal substrates. It was found that those WB epoxy primers could enhance corrosion protection as mid-coats to WB Zn-rich primers; when being used direct-to-metal, WB epoxy primers also exhibited good mechanical and adhesion properties that benefited the overall anticorrosion performances.

INTRODUCTION

Cashew Nutshell Liquid (CNSL) is a sustainable and non-food chain biomaterial that can be obtained as a by-product of the cashew industry.¹ CNSL is contained in the honeycomb structure of the cashew nutshell (shown in *Figure 1*), and is primarily composed of 60–70% anacardic acid, 10–20% cardols, 3–10% cardanols, and 2–5% 2-methylcardols.²

FIGURE 1—Cashew apple and nutshell.³



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Cardanol is the main component derived from CNSL via decarboxylation and extraction.¹ The chemical structure of cardanol is a pentadecadienyl phenol with a long aliphatic side chain that usually consists of a mixture of one, two, and three double bonds in a linear chain (illustrated in *Figure 2*). The unique and versatile structure of cardanol enables this natural oil to become a very important chemical building block for numerous bio-based products. As an example, phenalkamine products are made from the Mannich reaction of cardanol and different amines (illustrated in *Figure 3*). The long aliphatic side chain delivers excellent water resistance (hydrophobicity), flexibility, and low viscosity. The aromatic ring provides good chemical resistance while the phenolic hydroxyl contributes to superb adhesion to various substrates as well as fast ambient and low temperature cure.⁴

Typically, phenalkamines are used in solventborne and high solids epoxy coating systems in marine and protective coating applications.⁴ To meet more stringent government regulations and increasing requests for renewable and sustainable products, novel zero-VOC waterborne (WB) CNSL-based curing agents have been developed via stabilizing the cardanol-based structures in

water without the help of co-solvents.⁵ These new WB CNSL-based curing agents not only have high bio-contents (41%-55%), but also retain the unique performances from solventborne phenalkamine counterparts, such as fast cure, good early water resistance, excellent adhesion to various substrates, and high mechanical strengths.⁵

Additionally, the development of WB Zn-rich primer is a trend in the coatings industries. However, one of the biggest challenges of WB Zn-rich primer systems is how to solve the potential stability and safety issues caused by the reactions between zinc particles and water.⁶ One unique technique is to develop special water-free curing agents in which zinc particles can be easily dispersed to form zinc-containing pastes. Those water-free zinc pastes can have very good shelf stability and are also ready to use with various epoxy dispersions to provide good corrosion protection performances.⁶

This article presents the latest studies of using a new water-free CNSL-based curing agent to formulate 2K WB Zn-rich primer systems, and the advantages of using a bio-based material (referred to as Bio-M) in WB Zn-rich primer systems will be discussed. Furthermore, a novel, low-viscosity,

zero-VOC CNSL-based WB curing agent was formulated into various mid-coat systems with different epoxy dispersion resins. The mechanical and adhesion properties and anticorrosion performances of these mid-coat primers were investigated and are reported on here.

MATERIALS AND EXPERIMENTAL

In *Table 1*, the typical properties of three new CNSL-based WB curing agents, referred to as WB-A, WB-B, and WB-C, are listed.

In this study, five different solid epoxy dispersion resins, referred to as Resin 1, Resin 2, Resin 3, Resin 4, and Resin 5, were used. Their typical properties are listed in *Table 2*.

Linear dry time tests were carried out according to ASTM D5895-03. The clear (non-pigmented) coating systems were applied on 12 x 1 x 0.125 in. glass strips via an 8-mil drawn down bar. The glass strips were immediately placed on drying recorders that had been stored in a 25°C incubator. The styluses were lowered onto the wet coating to start the linear dry time tests.

The panels for cross-hatch adhesion tests (ASTM D3359) were prepared by applying the paint systems over QD-36 CRS panels via a 5-mil drawn down bar (*Figure 4*). The coating films were cured at room temperature (RT) for seven days before testing.

The WB Zn-rich primer systems were applied over different types of substrates via air spray. After seven days RT cure, the panels were evaluated for adhesion tape tests (ASTM D3359), Mandrel Bend tests (ASTM D522), impact test (ASTM D2794), and salt spray exposure (ASTM B117).

FIGURE 2—Average cardanol structure.

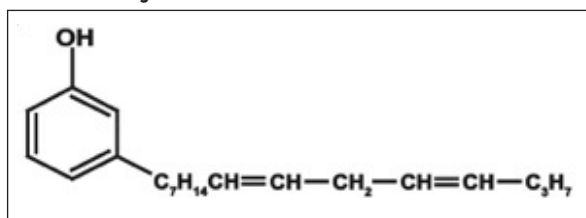


FIGURE 3—Example of phenalkamine structure.

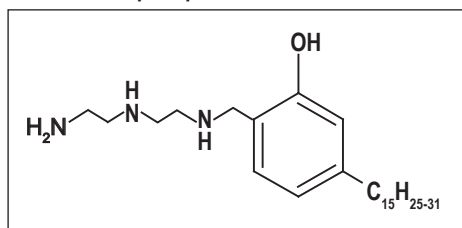
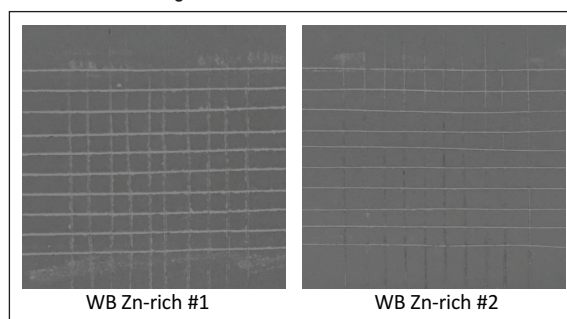


FIGURE 4—Panel images of cross-hatch adhesion tests.



RESULTS AND DISCUSSIONS

Part I: Waterborne (WB) Zn-rich Primer Study

To improve the shelf stability of WB Zn-rich primer systems, a water-free CNSL-based curing agent, WB-A, was developed. Its bio-content is calculated to

be about 41.5%. The non-pretreated zinc particles could be well dispersed into the WB-A side directly. By using this new water-free CNSL-based curing agent, several different WB Zn-rich primer systems were formulated. Two types of solvents were added to reduce the high viscosities (due to the high loading of zinc particles) as well as to help better film formations. In some of the WB Zn-rich

primer formulations, a natural bio-based low viscosity material (Bio-M, with 98% bio-content) was also added. The performances of CNSL-based WB Zn-rich primers, especially the anticorrosion properties, were evaluated and compared.

In Table 3, four different WB Zn-rich primer formulations are listed. WB Zn-rich #1 and #2 have similar formulations except that the WB Zn-rich #2 contains about 1.5% Bio-M. The percentages of zinc loading in dry film are 86.38% and 84.73% for WB Zn-rich #1 and WB Zn-rich #2, respectively. The PVC of WB Zn-rich #1 (50.84%) was higher than the one of WB Zn-rich #2 (46.80%) because of the presence of Bio-M. The low viscosity of Bio-M in WB Zn-rich #2 also helped with the viscosity reduction while maintaining even lower VOC (203.95 gm/l) than the one (217.44 gm/l) of WB Zn-rich #1.

In Table 4, test results for the mechanical properties of WB Zn-rich #1 and #2 are listed. Both WB Zn-rich primers showed good Mandrel Bend performance, with no cracks and delamination observed. It was noted that the WB Zn-rich #2 system exhibited better impact properties and adhesion performance (illustrated in Figure 4) in comparison to WB Zn-rich #1. It indicates that the addition of 1.5% Bio-M could improve the flexibility of WB Zn-rich primer systems as well as their adhesion to metal substrates.

For anticorrosion tests, WB Zn-rich #1 and #2 primer systems were air sprayed over blasted steel substrates (SA2.5). After seven days RT cure, the panels were placed in a Q-FOG chamber for salt spray test. The dry film thicknesses (DFT) were about 2 to 2.5 mils.

The images of WB Zn-rich #1 and #2 panels after 120-h salt spray exposure are shown in Figure 5. It can be seen that WB Zn-rich #1 system already had some rust on the panel surface, but the panel of WB Zn-rich #2 system was still intact. Some white zinc oxide products

TABLE 1—Waterborne Curing Agents: Typical Properties

PROPERTIES	WB-A	WB-B	WB-C
VISCOSITY AT 25°C (CPS)	1870	20000-55000	3000-18000
AMINE VALUE (MG KOH/G)	262	140-180	120-150
SOLIDS %	80	50	55-58
AHEW (AMINE HYDROGEN EQUIVALENT WEIGHT)	168	270	290
COLOR (GARDNER)	11	7	WHITE EMULSION
RECOMMENDED USE LEVEL (PHR, EEW 190)	60-68	105-130	107-152
WATER%	0	50	45
BIO-CONTENT%(BASED ON SOLIDS)	41.5	41.5	55.4

TABLE 2—Typical Properties of Solid Epoxy Dispersion Resins

SOLID EPOXY DISPERSIONS	PROPERTIES			
	VISCOSITY AT 25°C (CPS)	SOLID CONTENT (%)	EPOXY EQUIVALENT WEIGHT ^a	COLOR
RESIN 1	1000-15000	51-55	520-600	WHITE EMULSION
RESIN 2	300-1300	55-59	400-500	WHITE EMULSION
RESIN 3	500-5000	51-55	480-550	WHITE EMULSION
RESIN 4	2850	47	490	WHITE EMULSION
RESIN 5	1000-6000	52-54.5	500-600	WHITE EMULSION

(a) Based on solids.

TABLE 3—WB Zn-Rich Primer Formulations by Using WB-A Curing Agent

COMPONENTS	WB ZN-RICH #1	WB ZN-RICH #2	WB ZN-RICH #3	WB ZN-RICH #4
WB-A	1.98	1.95	2.81	2.64
DISPERSANT	0.99	0.97	1.43	1.35
DEFOAMER	0.06	0.06	0.11	0.11
ZINC DUST	69.19	68.13	67.80	63.73
BIO-M	0	1.54	0.56	0.53
SOLVENT 1	3.76	3.70	4.21	3.96
SOLVENT 2	0.59	0.58	0.87	0.82
FLASH RUST INHIBITOR	0.00	0.00	0.26	0.24
SUBTOTAL OF PART A	76.56	76.92	78.05	73.36
RESIN 1	15.63	15.39	/	20.74
RESIN 2	/	/	15.67	/
DI WATER	7.03	6.92	5.64	5.30
SOLVENT 1	0.78	0.77	0.63	0.59
SUBTOTAL OF PART B	23.44	23.08	21.95	26.64
TOTAL PART A & B	100.00	100.00	100.00	100.00
VOC (GM/L)	217.44	203.95	221.03	204.72
%WT NVM	80.08	80.39	81.11	78.83
% WT PIGMENT	69.19	68.13	67.80	63.73
% PVC	50.84	46.80	40.54	40.52
% ZN IN DRY FILM	86.38	84.73	83.62	80.86
EPOXY/AMINE	1.26	1.26	1.25	1.25

TABLE 4—Mechanical Properties of WB Zn-Rich Primers

SYSTEMS	WB ZN-RICH #1	WB ZN-RICH #2
MANDREL BEND	1/8 IN.	1/8 IN.
IMPACT (DIRECT/REVERSE)	56/4	120/40
CROSS-HATCH ADHESION (OVER QD-36 CRS)	4B	5B

FIGURE 5—Panel images after 120-h salt spray exposure.

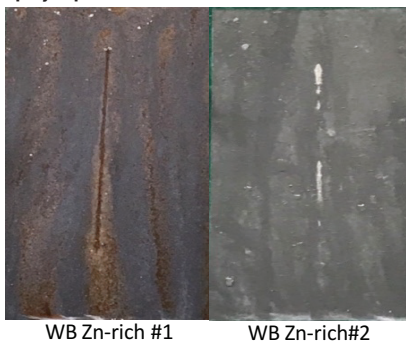


FIGURE 6—Panel images after 4000-h salt spray exposure.

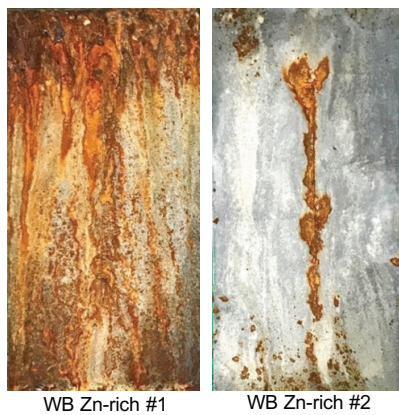


FIGURE 7—Panel images after 1200-h salt spray exposure.

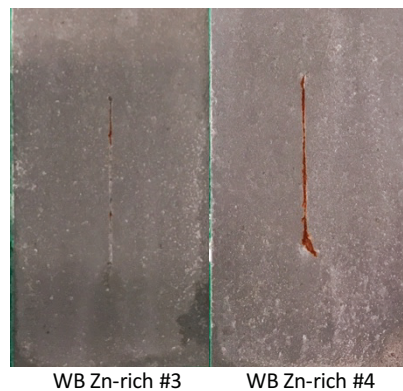


FIGURE 8—Panel images after 2400-h salt spray exposure (surface rusts were removed via scratch pad).



are observed on the panel surface of the WB Zn-rich #2 system, which indicated the efficient cathodic protection provided by zinc particles. In *Figure 6*, the images show the panels after 4000 h of salt spray testing. It can be seen that the WB Zn-rich #1 primer system has serious rust all over the panel, but the WB Zn-rich #2 primer system still provides good corrosion protection to most areas of the panel.

The comparison results between WB Zn-rich #1 and #2 primer systems suggested that the use of Bio-M in WB Zn-rich primer systems could offer several advantages. First, the low viscosity of Bio-M could help to reduce the viscosity of Zn-rich primer pastes without contributing any VOC. Second, Bio-M could help to improve the flexibility of coating systems, which is very important to Zn-rich primer systems due to the heavy loading of zinc particles. Third, Bio-M seems to help with the adhesion of WB Zn-rich coatings to metal substrates. Fourth, the hydrophobic nature of Bio-M could prevent WB Zn-rich primers from fast rust due to the improved water resistance. Fifth, it seems that the use of Bio-M material does not hurt electric conductivities among zinc particles since excellent cathodic protection of WB Zn-rich #2 was observed after 4000 h of salt spray testing.

Therefore, in *Table 3*, Bio-M was used in both WB Zn-rich #3 and #4 primers, but at lower content. WB Zn-rich #3 and #4 systems have similar formulations, but are combined with two different solid epoxy dispersions. By design, the PVCs of WB Zn-rich #3 and #4 were reduced to 40% to lower cost and viscosity. The test panels were also

air sprayed over SA 2.5 steel substrates and were placed in a salt spray test after seven days of RT cure. The DFTs of WB Zn-rich #3 and #4 were about 2 mils and 2.5 mils, respectively.

Figure 7 shows the panel images after 1200-h salt spray exposure. It can be seen that both WB Zn-rich #3 and #4 systems exhibit similar excellent corrosion resistance: no rust and blisters are observed on the panels surfaces, and only a little rust formed in the scribe lines. Also, the white zinc oxide products formed on the surfaces of WB Zn-rich #3 and #4 primers indicate that both WB Zn-rich primer systems provide good cathodic protection to the substrates.

After 2400-h salt spray exposure (shown in *Figure 8*), there were many rust spots and white zinc oxide products observed on the surfaces of the panels. After scribing and removing the surface rust via a scratch pad, it can be seen that WB Zn-rich #3 and #4 primer systems still provided good protection to metal substrates. No creep occurred along the scribe lines, and both primers still maintained excellent adhesion. (It was very hard to scratch the primers off from the steel substrates.) However, the WB Zn-rich #3 system showed more zinc oxide products and rust spots on the panel in comparison with the one from the WB Zn-rich #4 system. This might be due to the thinner film thickness of the WB Zn-rich #3 primer, or because a different type of solid epoxy dispersion, Resin 2, was used.

In general, Zn-rich primer systems have a very porous nature due to their high PVC (near or above CPVC) formulations. The high zinc particle

FIGURE 9—Panel images after 2300-h salt spray exposure (WB Zn-rich primer systems topcoated with a red iron oxide mid-coat).

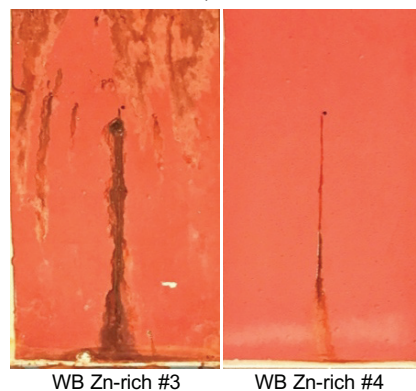


FIGURE 10—Panel images after scribe and wet adhesion testing.

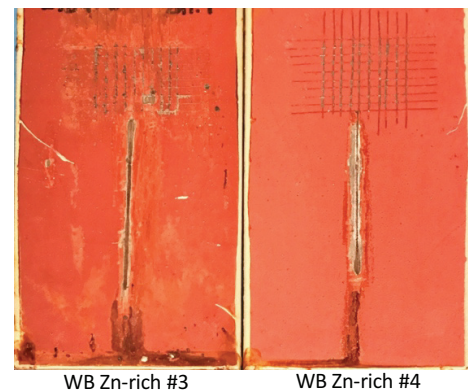


FIGURE 11—Mixing viscosity changes as a function of the percentage of added water.

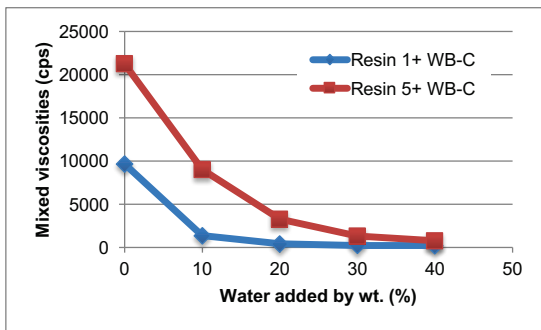
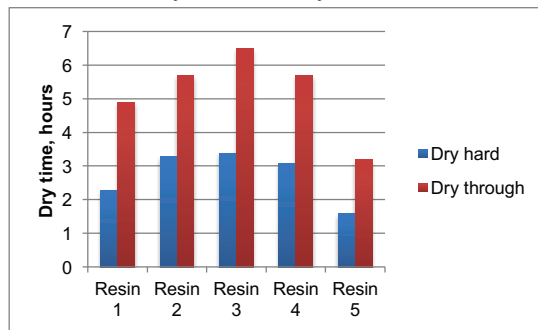


FIGURE 12—Linear dry time of various systems based on WB-C.



loads in the binder system can obtain better electrical conductivities among zinc particles as well as to the metal substrates; as a result, better cathodic protection can be achieved. However, porous Zn-rich primers normally do not have good barrier properties. Therefore, a multi-layer coating system that combines Zn-rich primer with a mid-coat and/or a topcoat can obtain the synergy of cathodic protection and barrier protection to achieve excellent and long-term corrosion resistance.

In this study, a red iron oxide WB mid-coat system (based on WB-B) was air sprayed over WB Zn-rich #3 and #4 systems. The dry film thicknesses of the mid-coats were about 1-1.5 mils. As shown in Figure 9, after 2300-h salt spray exposure, the WB Zn-rich #4 system still looked good: no rust and blisters on field, no creep along the scribe line, and very good wet adhesion (shown in Figure 10). The WB Zn-rich #3 system showed slightly worse performance than the WB Zn-rich #4 system, which might be due to the lower film thickness or the different type of solid epoxy dispersion, Resin 2, used.

In summary, the test results of various CNSL-based WB Zn-rich primers presented and discussed above suggest that: 1) the non-pretreated zinc particles could be easily dispersed into a water-free CNSL-based curing agent to form stable WB Zn-rich primers with VOC under 230 gm/l; 2) Bio-M, a high bio-content material, could improve the flexibility of WB Zn-rich primers as well as contribute to better adhesion; 3) CNSL-based curing agents could be used with different types of solid epoxy dispersions; and 4) CNSL-based WB Zn-rich primers could provide excellent

cathodic protection for metal substrates; when combined with WB mid-coats, long-term and excellent corrosion protection could be achieved.

Part II: WB Mid-Coat Systems Based on New WB-C Curing Agent

WB-C is the most recently developed CNSL-based WB curing agent that has 55.4% calculated bio-content. As shown in Table 1, zero-VOC WB-C has much lower viscosity in comparison to WB-B.

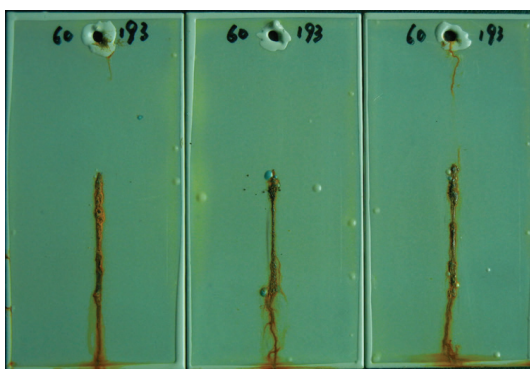
WB-C may have different initial viscosities when mixed with various solid epoxy dispersion resins. For example (as shown in Figure 11), the initial viscosities of WB-C mixed with Resin 1 or Resin 5 (@ stoichiometric ratio) were 9650 cps and 21250 cps, respectively; the viscosity of WB-C combined with Resin 5 was much higher than that of WB-C with Resin 1. However, by adding 30% water (which means the original solids percent of Resin 5 + WB-C system dropped from 54% to 45%), the viscosity of Resin 5 + WB-C system was reduced

from 21,000 cps to 1,280 cps. For the Resin 1 + WB-C system, the initial viscosity dropped from 10,000 cps to 1,350 cps by only adding 10% water. It suggests that WB-C has very good diluting power, regardless of the type of solid epoxy dispersion resin used.

CNSL-based WB-C curing agent has good compatibility with various solid epoxy dispersion resins. Figure 12 shows the dry time data (@25°C) of WB-C with five different solid epoxy dispersions at a stoichiometric ratio of 0.7. The solids percent of each clearcoat system was adjusted to 50%. It can be seen that WB-C had different dry hard times when used with different solid epoxy dispersions: the Resin 5 + WB-C system exhibited the fastest cure of 1.6 h dry hard time. Even the slowest system, Resin 3 + WB-C, still gave a quick 3.4 h dry hard time. It indicates that CNSL-based WB-C could provide fast cure properties to WB coating systems.

Figure 13 shows the panel images of a clear coating system based on Resin 1 and WB-C after 1200-h salt spray

FIGURE 13—Panel images of Resin 1 + WB-C clear coating system after 1200-h salt spray exposure.



exposure. The coating system was prepared at 0.7 stoichiometric ratio and 50% solids, and it contained no solvent, but some flash rust inhibitor to prevent quick rust during cure. Cold rolled steel (CRS) panels were used as the substrates; the DFT of the clear coatings was about 3.5 mils after seven days RT cure. It can be seen that there were only a few blisters on the test panels after a 1200-h salt spray test. It suggests that WB-C could provide good anticorrosion performances when just combined with solid epoxy dispersions.

Moreover, four low-VOC WB mid-coat systems were formulated based on WB-C curing agent and three different solid epoxy dispersions, as shown in Table 5. All four WB mid-coat systems had VOCs close to or less than 90 gm/l. Some performances, such as pot life, mechanical properties, adhesion to various metal substrates, and anticorrosion properties, were evaluated based on those four mid-coat systems.

The first two mid-coat systems (referred to as MC#1 and MC#2) were developed based on Resin 3 and Resin

4, respectively, and the final solids percents of MC#1 and #2 were about 60%. In this study, the pot lives of MC#1 and MC#2 systems were determined by two key performances: adhesion and anticorrosion properties. A common way to measure the pot life of a 2K solventborne epoxy system is to monitor viscosity changes. However, it is difficult to detect the true pot life of a 2K WB epoxy system just based on the viscosity increases. That is because WB epoxy systems might lose their key performances before any significant viscosity changes could be observed after mixing solid epoxy dispersions and WB curing agents.

Therefore, as shown in Table 6, after mixing the epoxy and curing agent parts for MC#1 and MC#2, the paint systems were drawn down over QD-36 CRS panels with a WFT of 8 mils at intervals of 0, 4, 7, 21, and 48 h of storage time (the paint mixture was kept in a glass bottle with a closed cap at RT during storage time). Cross-hatch adhesion tests were conducted after the panels were cured at RT for three days; another set of panels were placed into the Q-FOG chamber for a three-day salt spray exposure. From the test results listed in Table 6, it can be seen that both MC#1 and MC#2 systems showed excellent adhesion even after paint systems were stored for 48 h. However, salt spray results revealed that MC#1 system prepared after 21 h of storage time started to show blisters and rust; and the MC#2 system exhibited dense tiny blisters when the storage time was 48 h. These test results suggested that WB-C curing agent could formulate mid-coat primer systems with very long pot life that benefit coating applications.

In addition to offering long pot life, MC#1 and MC#2 mid-coat systems showed balanced mechanical properties as well as good adhesion to different types of substrates, as shown in Table 7. Both MC#1 and MC#2 had excellent Mandrel Bend properties. The MC#2 system exhibited better impact resistances in comparison to the MC#1 system. Since MC#1 and MC#2 systems had very similar pigment loading, solids percent and PVC percent, the difference in impact resistance results might come from the solid epoxy dispersion used.

Cross-hatch adhesions of MC#1 and MC#2 were evaluated over three

TABLE 5—WB Mid-Coat Formulations Based on WB-C

COMPONENTS	MC#1	MC#2	MC#3	MC#4
WB-C	8.76	8.50	9.33	8.45
RHEOLOGICAL ADDITIVE	0.00	0.00	0.15	0.13
DEFOAMER	0.11	0.10	0.13	0.12
PIGMENT 1	4.38	4.25	5.44	4.93
PIGMENT 2	8.76	8.50	3.63	3.29
INHIBITOR 1	7.88	7.65	8.16	7.40
INHIBITOR 2	0.70	0.68	1.03	0.94
FILLER 1	6.13	5.95	6.35	5.75
FILLER 2	10.51	10.20	9.07	8.22
FILLER 3	0.61	0.59	0.63	0.58
SOLVENT 1	0.88	0.85	0.73	0.66
SOLVENT 2	1.75	1.70	1.45	1.31
FLASH RUST INHIBITOR	0.25	0.24	0.22	0.20
WATER	12.70	12.32	6.53	5.92
SUBTOTAL OF PART A	63.40	61.53	52.85	47.88
RESIN 3	36.60	0.00	39.06	0.00
RESIN 4	0.00	38.47	0.00	0.00
RESIN 5	0.00	0.00	0.00	37.80
WATER	0.00	0.00	8.09	14.32
SUBTOTAL OF PART B	36.60	38.47	47.15	52.12
TOTAL PART A & B	100.00	100.00	100.00	100.00
VOC (GM/L)	88.00	90.20	86.94	84.15
% WT NVM	62.44	59.86	59.23	54.94
% VOL NVM	48.80	45.48	46.25	40.96
% WT PIGMENT	17.94	17.25	33.29	30.16
% PVC	36.77	37.93	30.84	30.62
EPOXY/AMINE	1.25	1.25	1.25	1.25

TABLE 6—Adhesion and Anticorrosion Performances of MC#1 and MC#2 Systems as a Function of Mixing Times

SYSTEMS	PROPERTIES	TIME AFTER MIXING RESINS AND WB-C				
		0 H	4 H	7 H	21 H	48 H
MC#1	CROSS-HATCH ADHESION	5B	5B	5B	5B	5B
	SALT SPRAY (3 DAYS)	EXCELLENT	EXCELLENT	EXCELLENT	BLISTERS, RUST	SERIOUS RUST
MC#2	CROSS-HATCH ADHESION	5B	5B	5B	5B	5B
	SALT SPRAY (3 DAYS)	EXCELLENT	EXCELLENT	EXCELLENT	EXCELLENT	DENSE TINY BLISTERS

different types of metal substrates: bare steel (smooth mill), galvanized steel, and AA 2024 T3. There was no pre-treatment for the bare steel panels; the panel surface of galvanized steel was wiped with acetone paper towels; and the panel surface of AA 2024 T3 was sanded via 220 grit sandpaper followed by an acetone rinse and paper towel cleaning. MC#1 and MC#2 systems were applied via air spray over metal panels. After seven days RT cure, adhesion tests were conducted. The DFT of the coating films was around 2 mils. Results listed in *Table 7* demonstrates that both MC#1 and MC#2 systems had excellent adhesion to different types of metal substrates. It verifies that, similar to solventborne phenalkamines, the new CNSL-based WB curing agent inherited the superb adhesion property that could further benefit corrosion protection performances.

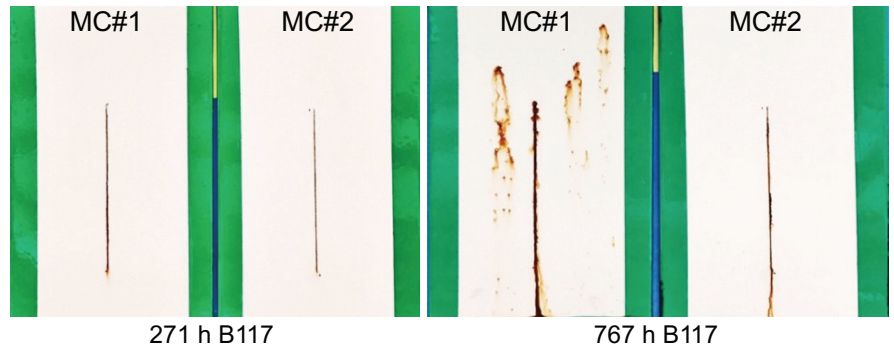
The anticorrosion performances of MC#1 and MC#2 systems were assessed as direct-to-metal (DTM) primers. The primer systems were air sprayed onto non-pretreated SA2.5 steel substrates. After seven days RT cure, the panels with DFT of 2–2.5 mils were placed in the salt spray chamber. In *Figure 14*, the two panels on the left represent MC#1 and MC#2 systems after 271 h of salt spray testing. There were no blisters observed on the panels’ surfaces, and almost no rust was formed along the scribe lines. With the longer salt spray exposure (two panels on the right in *Figure 14*), the MC#2 system still exhibited excellent anticorrosion properties with very few blisters and under 1mm creep near the scribe line. However, the MC#1 system had some rust and blisters on the coating film, and the creep along the scribe line was wider than the one of the MC#2 system. It seems that the Resin 3 used in the MC#1 system resulted in a little worse anticorrosion performance in comparison to the Resin 4 used in the MC#2 system. These test results suggest that WB-C could be used to formulate high performance primer systems that are suitable for DTM applications.

Figure 15 shows the panel image of a multi-coat system after 1685-h salt spray exposure. This multi-coat system consisted of a WB Zn-rich #4 primer topcoated with a MC#2 mid-coat. The DFTs of WB Zn-rich #4 primer and

TABLE 7—Mechanical and Adhesion Properties of MC#1 and MC#2

SYSTEMS	MC#1	MC#2
MANDREL BEND	1/8"	1/8"
IMPACT (DIRECT/REVERSE)	39/5	48/26
CROSS-HATCH ADHESION (QD-36 CRS PANEL)	4B	5B
CROSS-HATCH ADHESION (GALVANIZED STEEL PANEL)	5B	5B
CROSS-HATCH ADHESION (AA2024 T3)	5B	5B

FIGURE 14—Panel images of MC#1 and MC#2 systems after 271 and 767-h salt spray exposure.



MC#2 mid-coat were about 2.5 mils and 1.5 mils, respectively. After 1685-h salt spray exposure, there was no blister or rust observed on the panel field, and only some rust formed along the scribe line. The results confirmed that MC#2 mid-coat had excellent adhesion to WB Zn-rich primers and could enhance the long-term corrosion protection of WB Zn-rich primers by providing good synergy of barrier protection.

Part III: Wet-on-Wet Properties

Some industrial applications, such as transportation and agricultural construction and earth moving equipment segments, require WB primer systems to be quickly topcoated by polyurethane (PU) coatings even before the primers are fully cured. Usually, very short recoat times, e.g., 30 min or less, are given between applying two layers of coatings in those wet-on-wet applications. If the primer system has poor compatibility with the PU topcoat or is slow to cure, very often the PU topcoat will have a dieback issue, which means the PU topcoat loses its original high gloss and also has bad adhesion to the primer system.

In this study, the wet-on-wet topcoat performances were evaluated on two mid-coat primer systems, MC#3 and

MC#4, whose formulas were based on Resin 3 and Resin 5, respectively (listed in *Table 5*). Both MC#3 and MC#4 primer systems had VOC of less than 87 gm/l. Mid-coat primer systems, MC#3 and MC#4, were applied via air spray over CRS at a WFT of 2–2.5 mils. One set of panels was cured at RT for 30 min while another set of panels was baked at 60°C oven for 30 min. Then, a commercial 2K solventborne PU system was applied over the two sets of panels via air spray. After a 24-h RT cure, the glosses of the panels with two coats as well as their adhesions were measured (illustrated in *Figure 16*). In *Table 8*, the gloss data are listed and compared to the original gloss of the PU (PU applied over bare CRS with no primer underneath). It can be concluded that both MC#3 and MC#4 systems had high gloss retentions (>95%) and excellent adhesion (>=4B) with the commercial PU topcoat. It suggests that WB-C could achieve very good wet-on-wet properties regardless of which types of solid epoxy dispersion resins were used.

CONCLUSIONS

In this study, several stable WB Zn-rich primers were formulated by dispersing non-pretreated zinc particles into a water-free CNSL-based curing agent.

FIGURE 15—Panel image of WB Zn-rich #4 primer system topcoated with MC#2 mid-coat primer after 1685-h salt spray exposure.

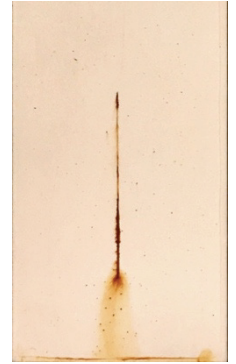
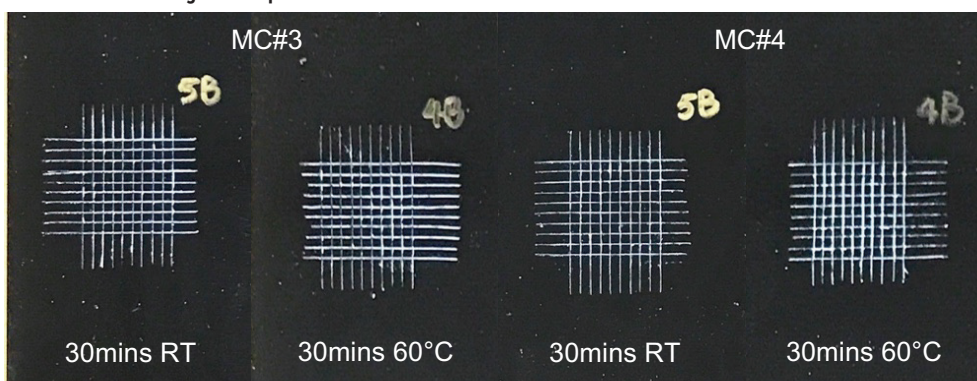


TABLE 8—Gloss Comparison

GLOSS @ 60°	MC#3		MC#4	
	30 MIN @ RT	30 MIN @ 60°C	30 MIN @ RT	30 MIN @ 60°C
ORIGINAL GLOSS OF PU	89.5	89.5	89.5	89.5
GLOSS OF TWO-COAT SYSTEM	86.9	86.0	85.3	86.5
GLOSS RETENTION	97.1%	96.1%	95.3%	96.6%
CROSS-HATCH ADHESION	5B	4B	5B	4B

FIGURE 16—Photo images of the panels after wet-on-wet adhesion tests.



With the addition of about 1% of high bio-content material, the WB Zn-rich primer system showed improved flexibility and adhesion. As a result, the new WB Zn-rich primers using the water-free CNSL-based curing agent exhibited excellent long-term cathodic protection even at lower zinc particle loads. When topcoated with a thin red iron oxide mid-coat, the CNSL-based WB Zn-rich primer achieved much better anticorrosion performances and superb wet-adhesion to metal substrates.

Furthermore, newly developed high performance WB primers based on a zero-VOC CNSL-based curing agent were evaluated as direct-to-metal primers at low film thickness. The results confirmed that the CNSL-based WB curing agent could provide mid-coat primers with very long pot life without sacrificing fast cure, balanced mechanical properties, and superb adhesion, which resulted in mid-coat primers with excellent anticorrosion performances.

When combined with CNSL-based WB Zn-rich primer, the new mid-coat primer could enhance the long-term corrosion protection even further.

Additionally, the fast cure properties of the new CNSL-based WB curing agent enabled the WB mid-coat systems to be recoated with a commercial PU topcoat after 30 min while maintaining high gloss and good adhesion.

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