# Replacement of zinc phosphating and e-coating by a one-step primer?

Puomi, P., Van Ooij, W.J., Yin, Z. and Seth, A., University of Cincinnati, Department of Chemical and Materials Engineering, Cincinnati, OH 45221-0012, USA

In previous research we have demonstrated that the commonly used pretreatment for automotive steels via zinc phosphating, can be replaced by simple treatments with solutions of organofunctional silanes without loss of performance in the standard corrosion tests. Now we report on a new development in which we have replaced both the phosphating step and the cathodic electrocoat system with one primer system. This particular primer is based on an epoxy-acrylate binder, organofunctional silane, crosslinker and anti-corrosion pigment. This primer can be denoted as a 2-in-1 primer, as no conversion coating is required. Bonding to the substrate is affected by the silane in the primer. Two versions of this primer were tested in an automotive coating system in different performance tests on electrogalvanized (EZG) steel, hot-dip galvanized (HDG) steel and on cold-rolled steel (CRS). The reference panels contained the same automotive coating on zinc phosphated and e-coated substrates.

The initial results are reported here. All panels had excellent dry and wet tape paint adhesion. The salt water immersion and salt spray test results of the test panels were comparable with those of the reference panels. In the Ford APGE test<sup>\*</sup> the new primer substrates tended to form more white rust in the scribe than the reference samples, which formed more red rust. A tentative mechanism for the high performance of the 2-in-1 primer will be presented.

For more information contact: Professor William J. van Ooij University of Cincinnati Department of Chemicals and Materials Engineering Cincinnati, OH 45221-0012, USA Phone: 513 556 3194 Email: wim.vanooij@uc.edu

<sup>\* &</sup>quot;APGE" is an arbitrary designation given by the Ford Motor Company to a particular type of accelerated corrosion test procedure designed to predict the likely extent of cosmetic corrosion, with the test results being reported in millimeters of creep and/or corrosion from a scribe through the painted surface tested, so that the lower numbered values are preferable (Reference: Sienkowski, *et al.*, U.S. Patent 5,900,073, (1996)).

## **1. Introduction**

The problems that this paper will discuss are those that exist in the finishing line in the automotive industry. Currently the finishing line comprises approximately of the following steps: alkaline cleaning, rinsing, activation, phosphating, rinsing, sealing (by chromate or non-chromate rinses), rinsing, drying, e-coating, baking, base coating, baking, topcoating and baking. A schematic of the process up to the the e-coat baking stage is shown in Fig. 1.



Figure 1. The pretreatment and e-coating steps of a typical finishing line in the automotive industry.

There is currently great interest in the automotive industry to simplify this process so as to include fewer steps and to eliminate the chromate in the seal rinse and the lead present in the e-coating process. Very few articles have, however, been published on efforts on either simplifying the automotive coating process or improving some particular step of the process by making it, e.g., more environmentally friendly. A few publications on the latter subject were found. Rink and Mayer<sup>1</sup> presented a water-borne basecoat system for vehicle refinishes in which the VOC content had been reduced to less than 420 g/l from 650-800 g/l, which is typical for solvent-borne basecoats. Lenhard et al.<sup>2</sup> described a two-pack water-borne amine-curable epoxy primer surfacer which performed convincingly in different performance tests. They also studied

the crosslinking behavior of this primer surfacer. Mager et al.<sup>3</sup> used organic-inorganic hybrid coatings based on polyfunctional silanols to increase a conventional automotive clear coat's abrasion resistance, acid resistance and anti-adhesive properties.

Work on the former subject, i.e., simplifying the automotive finishing line has been done in our laboratory. We have earlier proposed a silane-based replacement for the zinc phosphating pretreatment in the automotive finishing line<sup>4</sup>. It is well-known that silane-based treatments are environmentally attractive and are also much simpler than the phosphating processes. They comprise of only three steps: alkaline cleaning, rinsing and silane dip or spray<sup>4-8</sup>. While such novel treatments are not yet used in the automotive industry, at least to our knowledge, they are already used in the coil coating industry. We have earlier also discussed a passivation treatment that can be deposited on HDG steel sheet in the galvanizing line and then the sheet can be primed and top-coated in the automotive finishing line<sup>9</sup>. The passivation treatment has been studied separately<sup>9</sup> and with an e-coat<sup>10</sup>. In the latter publication we also presented results on a 2-in-1 epoxy-based primer as replacement for the zinc phosphating pretreatment and e-coating in an automotive coating system. The primer coating is chromate, lead- and fluoride-free; it has low-VOC and is loaded with chromate-free anti-corrosion pigments which can provide scribe protection. With the superprimer in place of the phosphating and e-coating steps, the entire finishing process would consist of fewer steps, comprising of alkaline cleaning, rinsing, superprimer application, drying at moderate temperatures, base coating, baking, topcoating and baking.

In this paper we present new results on an improved superprimer in an automotive coating system. This superprimer is based on an epoxy-acrylate binder system, a bis-sulfur silane and zinc phosphate pigment. This primer was compared on three different substrates with a commercially available automotive coating system containing a tri-cation pretreatment, an electrocoat and a typical automotive coating finish.

## 2. Experimental

## 2.1 Substrate

The cold-rolled steel (CRS), the electrogalvanized (EZG) and hot-dip galvanized (HDG) steel panels were all obtained from ACT Laboratories, Midland, MI.

## 2.2 Coatings and panel preparation

Two versions of the epoxy-acrylate primer were tested in this study. The first version of the primer is based on proprietary formulations.<sup>\*\*</sup> The second version is based on another proprietary mix.<sup>\*\*\*</sup> Both primers contained the same bis-sulfur silane; bis(3-triethoxysilylpropyl) tetratsulfane from GE Silicones, Friendly, WV and the Alfa Aesar zinc phosphate from Johnson Mathey, Ward Hill, MA. Before superprimer application the metal panels were thoroughly de-

<sup>\*\*</sup> ECO-CRYLTM 9790 acrylic resin and EPI-REZTM WD-510 epoxy, Hexion Specialty Chemicals, Houston TX.

<sup>\*\*\*</sup> MaincoteTM AE-58 acrylic resin, Rohm & Haas, Philadelphia, PA and Daubond 9010W55 epoxy, Daubert Chemical Company, Chicago, IL.

greased, alkaline cleaned, rinsed and blown dried with pressurized air. The first epoxy-acrylate primer was applied by draw-down bar and the second version was sprayed on using a NB high-volume low-pressure (HVLP) spray gun from the Wagner Corporation, Minneapolis, MS. Both primer coatings were cured at room temperature (RT).

The commercially available automotive coating consisted of a melamine-polyester primer surfacer, a melamine-acrylic base coat and an acrylic-isocyanate clear topcoat. The superprimed panels were coated with the same base coat and clear topcoat as the automotive reference samples. The reference panels were also degreased and alkaline cleaned, after which they were pretreated with a standard Zn/Ni/Mn crystalline phosphate pretreatment. After phosphating the panels were electrocoated and the automotive surface finish described was applied to the panels. The panel descriptions are summarized in Table 1, including the dry film thicknesses (DFT) of the coatings.

 Table 1. Panel descriptions of the test and reference panels, including the dry film thicknesses (DFT) of the coatings.

Superprimed automotive samples	Automotive reference samples
No pretreatment	A standard automotive pretreatment
Superprimer, DFT ~ 0.25 mils	Primer surfacer, DFT ~ 1 mil
On both: same basecoat, DFT ~ 1 mil	
On both: same clear topcoat, DFT $\sim 2$ mils	

## 2.3 Characterization and testing

In this paper, the performance results of the epoxy-acrylate primer in the described automotive coating are first reported and then a tentative mechanism for the performance of the primer will be presented. The panels were tested in the following tests:

- ASTM D 3359-97 tape adhesion test both dry and wet adhesion (after 10 days immersion in DI water)
- Water immersion test with bare cut edges
- ASTM D 714 3.5 wt.-% NaCl solution immersion test
- FORD AGPE test
- ASTM B-117 salt spray test

The Ford AGPE test (also referred to as the Ford test in this paper) is a cyclic accelerated corrosion test including three cycles which are: 1) 15 minutes immersion in 5 % NaCl solution at room temperature; 2) 105 minutes ambient drying and 3) 2 hours in 90° humidity at  $60^{\circ}C^{11}$ . During the Ford AGPE test and the salt spray test the specimens were periodically removed from the chambers and EIS measurements were taken using handheld corrosion sensors and a Gamry PC-4 potentiostat. These sensors allowed the EIS measurements to be taken under ambient conditions instead of immersion, which is usually required for traditional EIS.

The epoxy-acrylate primer coating itself has been characterized extensively with various sophisticated tools<sup>12-13</sup>. For the mechanism evaluation the primer was studied by scanning electron microscope combined with energy dispersive X-ray analysis (SEM/EDX), water/electrolyte

uptake measurements and Fourier transform infrared (FTIR) spectroscopy. The exact measurement conditions for the techniques mentioned have been described elsewhere<sup>12</sup>.

## 3. Results and discussion

#### 3.1 Salt water immersion test results

Of the tests used, only the salt water immersion, Ford and salt spray test were able to establish differences among the samples. The adhesion test only showed that all samples had excellent adhesion. The water immersion test results just showed that there is a huge difference in the performance between CRS panels and others, but this test could not distinguish between the differently coated samples on a specific substrate. The huge difference between CRS panels and others could also be seen from the salt water immersion test results, which are shown for CRS panels in Fig. 2 and EZG panels in Fig. 3.



Figure 2. Salt water immersion test results of CRS panels after 7 weeks; a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference.



Figure 3. Salt water immersion test results of EZG panels after 3 months; a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference.

The CRS panels were kept in the salt water immersion test only for 7 weeks. After the test any loose paint at the scribes was scraped off. As can be seen from Fig. 2, the first epoxy-acrylate and the reference panel are very similar when it comes to the extent of red rust in the scribes. The scribes of the second epoxy-acrylate seem slightly worse, but the surface appearance of the coating was better on this sample than on the first epoxy-acrylate, which showed slight blistering of the coating. The EZG and HDG steel panels were kept in the salt water for 3 months. When the images presented in Fig. 3 are compared with the ones shown in Fig. 2, one can clearly see the difference in substrate performance. The scribes of the EZG panels hardly show any red rust even after 3 months of salt water immersion test. After the test the superprimed EZG panels showed blisters here and there. The blisters were, however, not very clearly visible after the panels had dried. Therefore, they cannot be distinguished easily in Fig.s 3a and 3b. The performance of the HDG steel panels in the salt water immersion test were almost exactly the same as for the presented EZG panels.

## 3.2 Ford test results

The CRS panels were exposed to the Ford AGPE test for 38 cycles, whereas the EZG and HDG panels were exposed to the Ford test for 50 cycles. The CRS panel images after the Ford test are shown in Fig. 4 and the HDG panels are shown in Fig. 5.



Figure 4. Ford test results of CRS panels after 38 cycles; a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference.



Figure 5. Ford test results of HDG steel panels after 50 cycles; a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference.

The replica panels had very similar performance in the Ford test. The pictures chosen for Figs. 4 and 5 represent the performance of each sample. As can be seen from Fig. 4, the scribes of the second epoxy-acrylate were slightly better than for the two other CRS panels and the surface of the second epoxy-acrylate sample was also better than for the first. However, in Fig. 4b, slight blistering very close to the scribe can be detected. It seems that when salt water or humidity is able to come in contact with the epoxy-acrylate superprimer underneath the automotive coating, it is prone to blistering. Here again, when the images presented in Fig. 5 are compared with the ones shown in Fig. 4, one can clearly see the difference in substrate performance. The scribes of the HDG steel panels in Fig. 5 hardly show any red rust after 50 Ford test cycles. Some blistering close to the scribes were observed for the superprimed HDG steel panels exposed to Ford test. In this test the first epoxy-acrylate showed slightly more blistering than the second version. The results of the EZG and HDG panels in the Ford test were again very similar, i.e., analogous to the salt water immersion test results.

During the Ford test, EIS measurements were taken periodically on the coating away from the scribe. The impedance and the phase angle plots as a function of frequency for the CRS samples are shown in Figs. 6 and 7, respectively.



Figure 6. The impedance as a function of frequency for the a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference on CRS.

As can be seen from Figs. 6 a) to c), the impedance curve of the exposed coating does not change during exposure to the Ford test. It is mainly the scribed part of the CRS panel that deteriorates due to the corrosion reactions of the steel, which is exposed to the aggressive environments of the test through the scribe.



c)

Figure 7. The phase angle as a function of frequency for the a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference.

We have noticed that sometimes when coating systems are exposed to corrosive environments, one cannot detect any early changes in the coating by observing it or by comparing impedance data of the coating. Sometimes the drop in the phase angle in the low frequency range is the most sensitive method to detect early deterioration of the coating in accelerated corrosion tests or especially during early stages of outdoor exposure testing.

Figures 7 a) to c) show, however, that there is no change in the phase angle curves of the CRS samples during exposure to the Ford test. The phase angle remains high between 80° to 90° throughout the frequency range on all samples. The impedance and phase angle results in the Ford test of the coatings on the EZG and HDG steel panels gave very similar results as on the CRS panels. Figure 8 presents the impedance results of the coatings containing the new epoxy-acrylate primer on all three substrates during Ford test.



Figure 8. Impedance results of the coatings containing the second epoxy-acrylate primer on all three substrates during the Ford test.

As can be seen from Fig. 8, the substrate does not affect the impedance values of the coating during Ford testing ( $\leq$  50 cycles).

#### 3.3 Salt spray test results

The panels were also exposed to ASTM B-117 salt spray testing even if the salt spray test might not be the most suitable test to test these coating systems. The scans of the CRS panels after 1250 hrs of salt spray testing are shown in Fig. 9.



a)

Figure 9. Salt spray test results of CRS panels after 1250 hours a) old epoxy-acrylate, b) new epoxy-acrylate and c) automotive reference.

Figure 9 shows a similar trend as the Ford results in Fig. 4; the scribe of the second epoxy-acrylate sample looks slightly better than for the two other samples. However, Fig. 9b) shows again, slight blistering near the scribe in the left upper corner of the scan.

The red rust formation in the scribes on all three samples in the salt spray test (Fig. 9) is quite different from the red rust formation in the Ford test (Fig. 4). This is most probably due to the fact that in the salt spray test when the samples are exposed to a continuous mist of salt water the red rust is not allowed to dry and form less soluble or more passive corrosion products such as in the cyclic Ford test. Therefore, the red rust formed in the scribes during salt spray testing has no chance to "recover" and just keeps on forming, which results in the bleeding pattern. The red rust formed in the cyclic Ford test has a chance to dry during the 105 minute ambient drying cycle. This is most likely the reason why the red rust in the scribes during Ford test is formed in small lumps, from which the red rust does not bleed off in the same extent as from the scribes in the salt spray test. Locally, where the red rust lumps have been formed they might in fact slightly suppress further red rust formation in that particular spot.

As the scans in Figs. 2 and 9 are compared with each other, it can be concluded that during continuous salt water immersion, of about 7 weeks, the red rust formation is significantly less than during about 7 weeks of salt spray testing (1250 hrs is about 7 weeks).

The difference in substrate performance was most notable in the salt spray test. The EZG and HDG steel panels were kept in ASTM B-117 for 1750 hours and almost nothing happened to the scribes. No red rust formed in the scribes during the 1750 hours. The superprimed EZG and HDG steel panels showed slight blistering close to the scribe, but otherwise the ASTM B-117 results of these panels were acceptable along with the EIS results of the coatings on them.

#### 3.4 The corrosion protective mechanism of the epoxy-acrylate superprimer

Figure 10 shows the SEM micrograph of the cross-section of the epoxy-acrylate primer on a metal surface. As can be seen from Fig. 10, the primer layer comprises three distinct layers. Closest to the metal there is a layer rich in silane. The middle of the coating consists of a resinsilane-particle layer. The cross-section was analyzed by SEM/EDX and the primer film by FTIR<sup>12</sup>. These results showed that the acrylate interacts with the silane forming an acrylate-siloxane layer, which situates in the middle of the coating, where also the zinc phosphate particles are incorporated. The epoxy, however, does not interact much with the other ingredients except for the crosslinker. Therefore, the epoxy forms virtually a layer of its own on top of the acrylate-siloxane-zinc phosphate layer.

The water and electrolyte uptake results showed that the epoxy layer of the coating is hydrophobic and the acrylate-siloxane layer is hydrophilic. There is, however, good interfacial adhesion between these two layers due to the silane present in the acrylate-siloxane layer. When the entire coating on aluminum is scribed and immersed in the 3.5 wt.-% NaCl solution, the ions of the solution  $Na^+$ ,  $Cl^-$ ,  $OH^-$  and  $H^+$  start to attack all layers of the coated metal. As the epoxy layer is hydrophobic, hardly any water or electrolyte will be able to penetrate into this layer of the coating, but as the acrylate-siloxane layer is hydrophilic, the water including the ions are able to penetrate into the middle layer of the coating. As this happens, the zinc phosphate pigment particles of the acrylate-siloxane layer are able to actively leach out into the salt water that surrounds the scribe. The phenomena described is presented schematically in Fig. 11.



Figure 10. The SEM cross-section of the epoxy-acrylate coating on the metal after 30 days of salt immersion testing.



**Figure 11.** Principle of the corrosion inhibiting mechanism of the acrylate-epoxy-silane superprimer containing the zinc phosphate pigments, which protect the metal on-demand.

As shown in Fig. 11 the zinc phosphate leached out into the scribe forms a saturated solution of  $Zn_3(PO_4)_2$  in the 3.5 wt.-% NaCl solution and thereby prevents any further ingress of electrolyte into the coating. The bis-sulfur silane film close to the metal protects the metal from

the electrolyte by forming a hydrophobic network of polysiloxane as the unhydrolyzed ethoxy groups of the silane are able to hydrolyze in the presence of water and react with each other forming a protective film of siloxane, Si-O-Si, close to the metal. If the water in the scribe is removed, no film is formed in the scribe, as most of the zinc phosphate along with the sodium and chlorine is washed away from the scribe.

The corrosion protection mechanism of the epoxy-acrylate coating, which is selfassembled into layers after depositing it from a water-borne dispersion is unique, as the chemistry of the coating facilitates the leaching of the zinc phosphate on-demand, when the coating is scribed and attacked by an electrolyte.

Taking into consideration the corrosion protective mechanism of the primer film, it is fairly easy to understand that when the primer is applied under an automotive topcoat finish on a panel which is scribed and attacked by corrosion, this may lead to slight blistering in the immediate vicinity of the scribe, as observed in the corrosion performance tests. The hydrophilic acrylate-siloxane-zinc phosphate layer attracts water and electrolytes, which enables the leaching of the zinc phosphate. The unhydrolyzed ethoxy groups of the bis-sulfur silane protect the interface by hydrolyzing and condensing to siloxane. However, after prolonged exposure to wet conditions these ethoxy groups are consumed and the water absorbed by the intermediate hydrophilic layer will eventually hydrolyze the siloxane back to hydrophilic silanol groups. This is when the intermediate layer may swell and slightly blister the topcoat finish. When the film is let to dry, siloxane is again formed in the intermediate layer and the blisters seem to disappear as observed when the samples were allowed to dry after the corrosion performance tests.

#### 4. Summary

The results presented clearly show that the performance of the samples prepared with the proposed technology is promising compared with the samples prepared with the commercially available state-of-the art technology. As expected the substrates performed differently. Overall the superprimed panels performed comparable with the reference panels on CRS. On EZG and HDG steel the reference panels performed better than the superprimed panels. An issue, which requires slight improvement is the tendency of the epoxy-acrylate primers to blister the automotive topcoat finish when in contact with salt water through a scribe, particularly on EZG and HDG steel. This tendency is milder for the second epoxy-acrylate primer compared with the first one. If the epoxy-acrylate primer can be improved in respect of the blistering tendency, then it will be a competitive candidate in challenging the conventional automotive coating technology. The benefits of the proposed technology are that it consists of significantly fewer steps than the current automotive coating process. Virtually no pretreatment is needed before primer coating, whereas the current process consist of pretreatment and e-coating, both including multiple steps before the automotive topcoat finish can be applied on the vehicle.

The epoxy-acrylate primer layer deposited from a water-based formulation has a unique composition as it self-assembles to a three-layer coating. The intermediate silane-containing layer is hydrophilic in nature and allows the zinc phosphate to leach out on-demand and protect the coating system when it is damaged and exposed to a corrosive environment. However, this

hydrophilic layer might also be the cause of the blistering of the superprimed automotive coatings after prolonged exposure to wet corrosive conditions.

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