Replacement of Zinc Phosphating and E-Coating by a One-Step Primer?

by P. Puomi, W.J. Van Ooij,[*] Z. Yin and A. Seth
University of Cincinnati
Department of Chemical and Materials Engineering
Cincinnati, OH 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,[**] 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.

Keywords: Zinc phosphate replacements, E-coat replacements, organofunctional silanes, automotive primers

Introduction

The problems that this paper will discuss are those that exist in the finishing line in the automotive industry. Currently, the finishing line is comprised 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 diagram of the process up to the e-coat baking stage is shown in Fig. 1.

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[1] 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 to 800 g/L, which is typical for solvent-borne basecoats. Lenhard, et al.[2] 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.[3] 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.[4] It is well-known that silane-based treatments are environmentally attractive and are also much simpler than the phosphating processes. They are comprised of only three steps: alkaline cleaning, rinsing and silane dip or spray.[4-8] 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.[9] The passivation treatment has been studied separately[9] and with an e-coat.[10] 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, comprised 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.

_____

[*] **Corresponding author:**
Professor William J. van Ooij
University of Cincinnati
Department of Chemicals and Materials Engineering
Cincinnati, OH 45221-0012
Phone: (513) 556-3194
Email: wim.vanooij@uc.edu

[**] "APGE," or "Arizona Proving Ground, Experimental" test, is a 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)].

Experimental

Substrate

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

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.[***] The second version is based on another proprietary mix.[†] 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 degreased, alkaline cleaned, rinsed and blow 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, MN. Both primer coatings were cured at room temperature.

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.

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 as follows:

- 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

_____

[***] ECO-CRYL™ 9790 acrylic resin and EPI-REZ™ WD-510 epoxy, Hexion Specialty Chemicals, Houston TX.
[†] Maincote™ AE-58 acrylic resin, Rohm & Haas, Philadelphia, PA and Daubond 9010W55 epoxy, Daubert Chemical Company, Chicago, IL.

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 min immersion in 5% NaCl solution at room temperature; (2) 105 min ambient drying and (3) 2 hr in 90% humidity at 60°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.[12-13] For the mechanism evaluation, the primer was studied by a 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.[12]

Results and discussion

Salt water immersion test results

Of the tests used, only the salt water immersion, Ford and salt spray tests 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 was 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.

The CRS panels were kept in the salt water immersion test only for seven 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 were very similar when it comes to the extent of red rust in the scribes. The scribes of the second epoxy-acrylate seemed 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 three 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 showed any red rust even after three months of salt water immersion. 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 Figs. 3a and 3b. The performance of the HDG steel panels in the salt water immersion test were almost exactly the same as for the EZG panels.

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

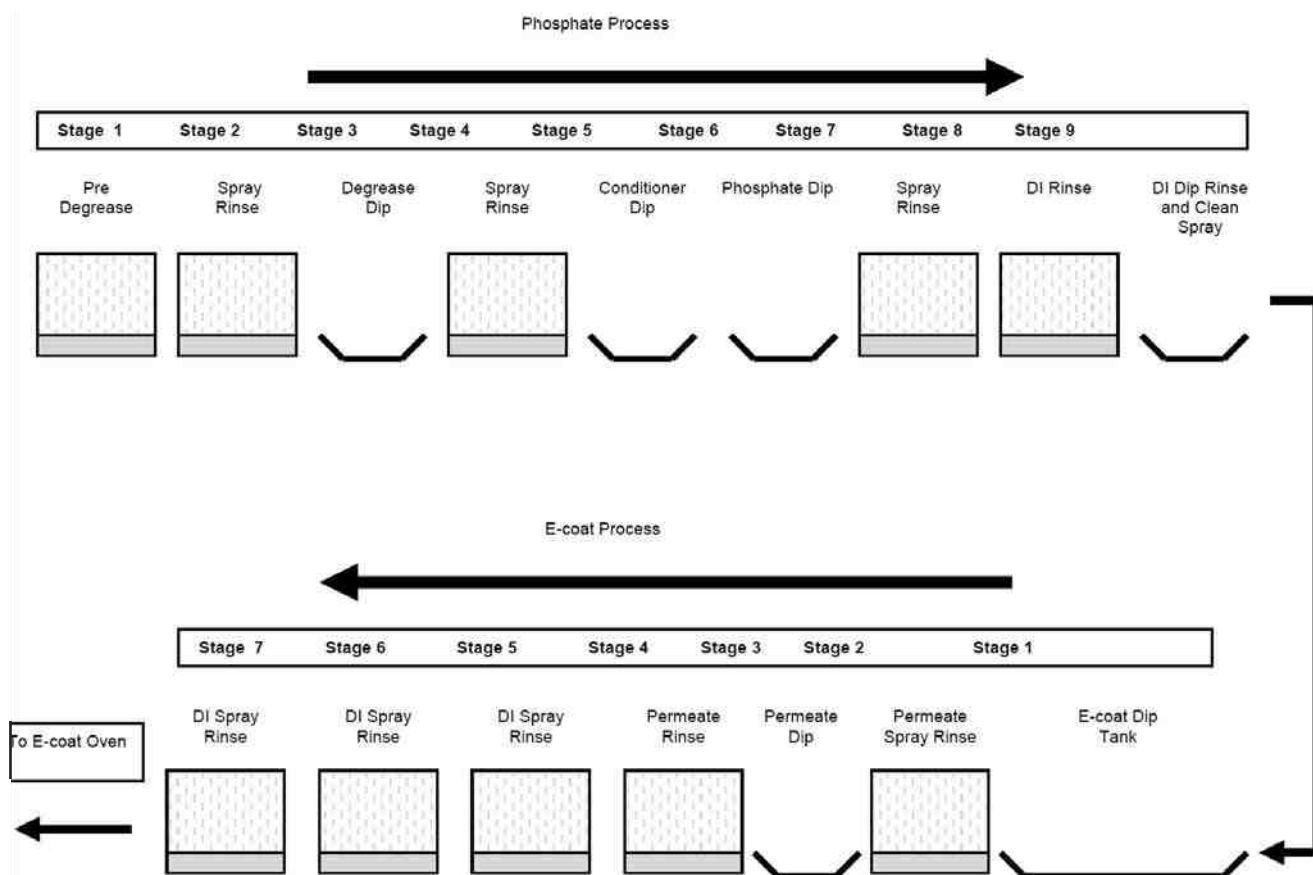| Superprimed automotive samples	Automotive reference samples
No pretreatment	A standard automotive pretreatment
Superprimer, DFT ~ 0.25 mils	Primer surfacer, DFT ~ 1 mil
On both: same basecoat, DFT ~ 1 mil	
On both: same clear topcoat, DFT ~ 2 mils	

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

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.

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 was 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.

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

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 7a thru c show, however, that there was no change in the phase angle curves of the CRS samples during exposure to the Ford test. The phase angle remained 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 results very similar to those 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. As can be seen, the substrate did not affect the impedance values of the coating during the Ford testing (≤ 50 cycles).
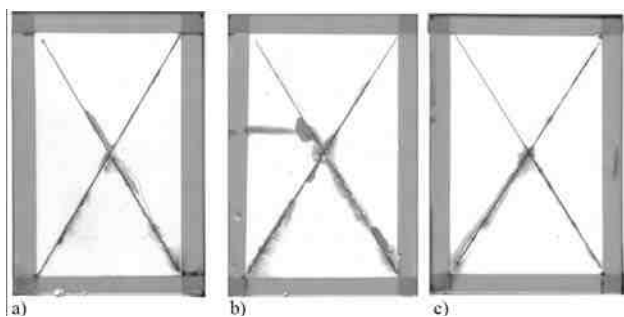
Figure 2—Salt water immersion test results of CRS panels after seven weeks: (a) first epoxy-acrylate, (b) second epoxy-acrylate and (c) automotive reference.
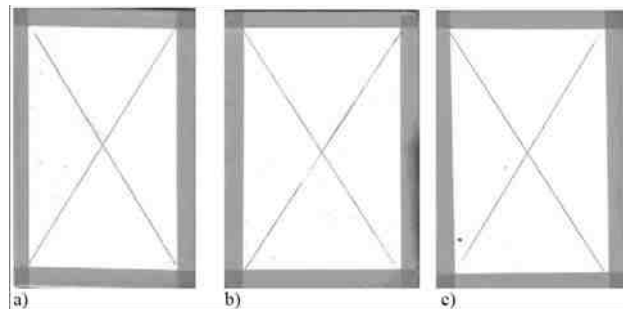

Figure 3—Salt water immersion test results of EZG panels after three months: (a) first epoxy-acrylate, (b) second epoxyacrylate and (c) automotive reference.
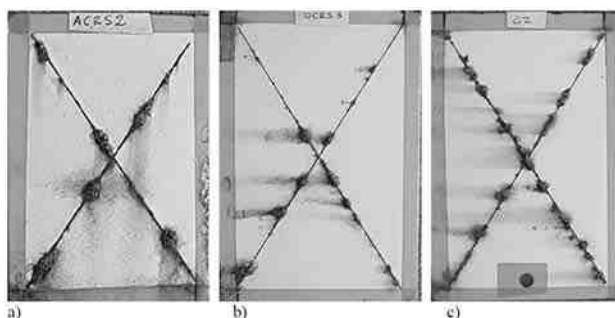

Figure 4—Ford test results of CRS panels after 38 cycles: (a) first epoxy-acrylate, (b) second epoxy-acrylate and (c) automotive reference.
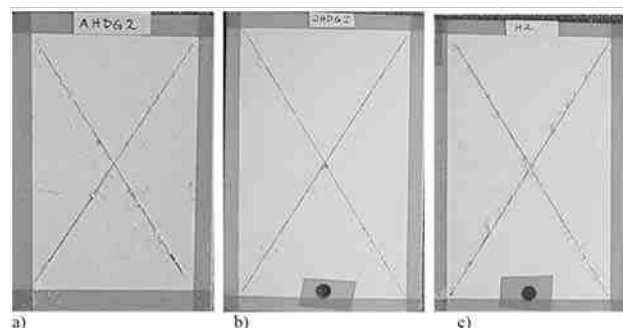

Figure 5—Ford test results of HDG steel panels after 50 cycles: (a) first epoxy-acrylate, (b) second epoxy-acrylate and (c) automotive reference.

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 hr of salt spray testing are shown in Fig. 9.

Figure 9 shows a trend similar the Ford results in Fig. 4. The scribe of the second epoxy-acrylate sample looked slightly better than 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-min ambient drying cycle. This is most likely the reason why the red rust in the scribes during Ford test were formed in small lumps, from which the red rust did not bleed off to 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 seven weeks, the red rust formation was significantly less than during about seven weeks of salt spray testing (1250 hr is about seven 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 hr and almost nothing happened to the scribes. No red rust formed in the scribes during the 1750 hr. The superprimed EZG and HDG steel panels showed slight blistering close to the scribe, but otherwise the ASTM B-117 results were acceptable along with the EIS results of the coatings.

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, the primer layer consists of three distinct layers. Closest to the metal is a layer rich in silane. The middle of the coating consists of a resin-silane-particle layer. The cross-section was analyzed by SEM/EDX and the primer film by FTIR.[12] These results showed that the acrylate interacted with the silane, forming an acrylate-siloxane layer, situated in the middle of the coating, where the zinc phosphate particles are also incorporated. The epoxy, however, did not interact much with the other ingredients except for the crosslinker. Therefore, the epoxy virtually formed 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 was hydrophobic and the acrylate-siloxane layer was hydrophilic. There was, however, good interfacial adhesion between the two layers due to the silane present in the acrylate-siloxane layer. When the entire coating on aluminum was scribed and immersed in the 3.5 wt% NaCl solution, the ions of the solution Na^+, Cl^-, OH^- and H^+ began to attack all layers of the coated metal. As the epoxy layer was hydrophobic, hardly any water or electrolyte was able to penetrate into this layer of the coating, but as the acrylate-siloxane layer was hydrophilic, the water including the ions could penetrate into the middle layer of the coating. As this happened, the zinc phosphate pigment particles of the acrylate-siloxane layer could actively leach out into the salt water that surrounded the scribe. The phenomena described are presented schematically in Fig. 11.

As shown in Fig. 11 the zinc phosphate leached out into the scribe formed a saturated solution of $Zn_3(PO_4)_2$ in the 3.5 wt% NaCl solution and thereby prevented any further ingress of electrolyte into the coating. The bis-sulfur silane film close to the metal protected the metal from the electrolyte by forming a hydrophobic network of polysiloxane as the unhydrolyzed ethoxy groups of the silane were 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 was removed, no film formed in the scribe, as most of the zinc phosphate along with the sodium and chlorine was washed away from the scribe.

The corrosion protection mechanism of the epoxy-acrylate coating, which is self-assembled 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.
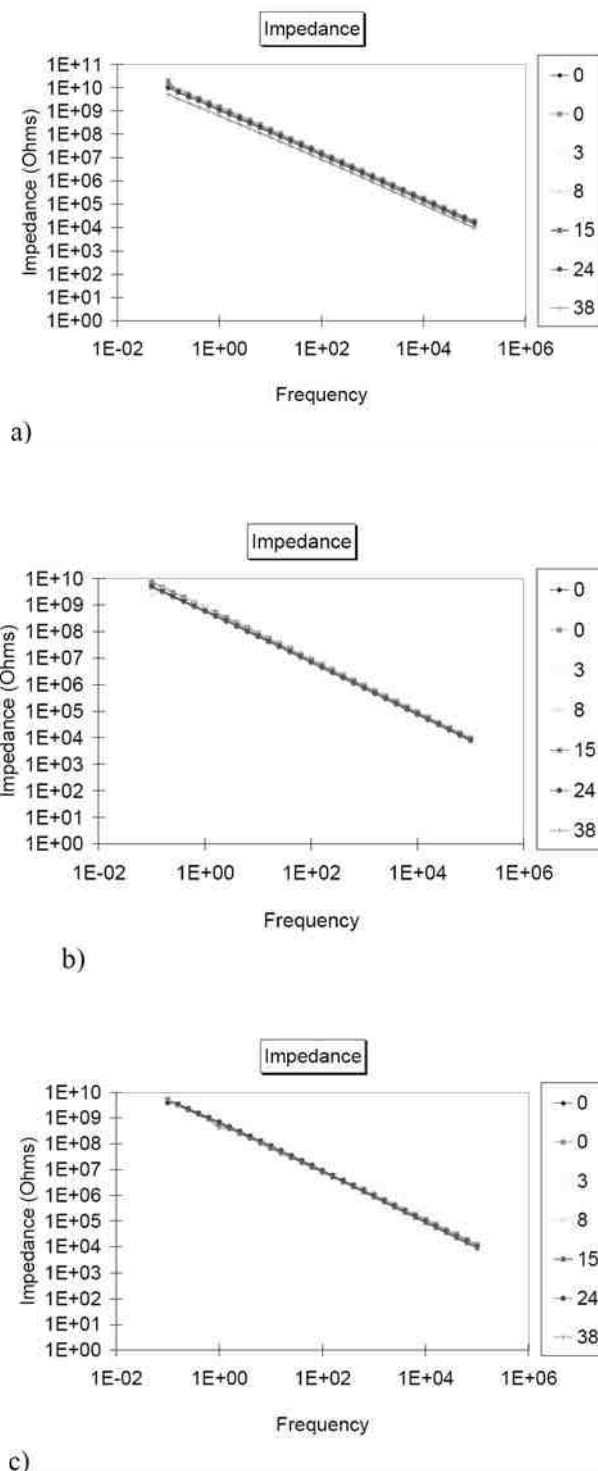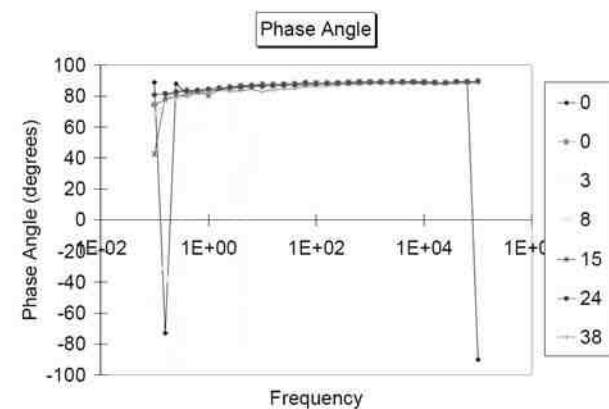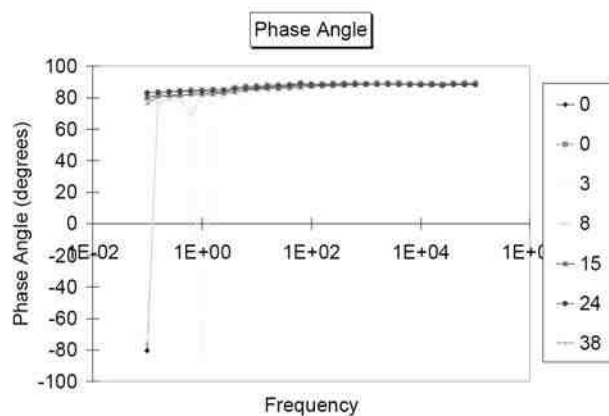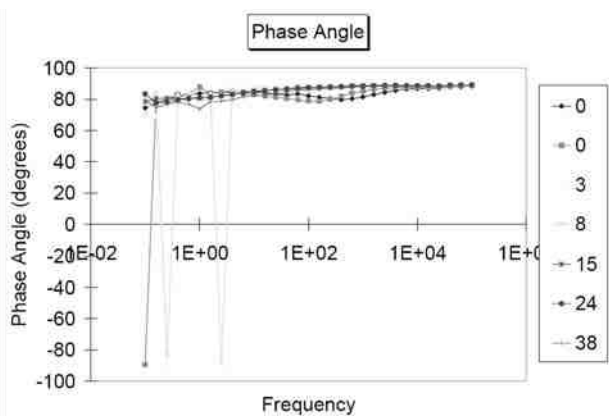

a)

b)

c)

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.

a)

b)

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.
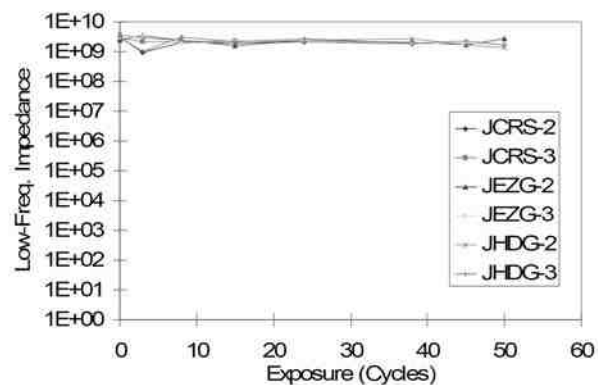

Figure 8—Impedance results of the coatings containing the second epoxy-acrylate primer on all three substrates during the Ford test.
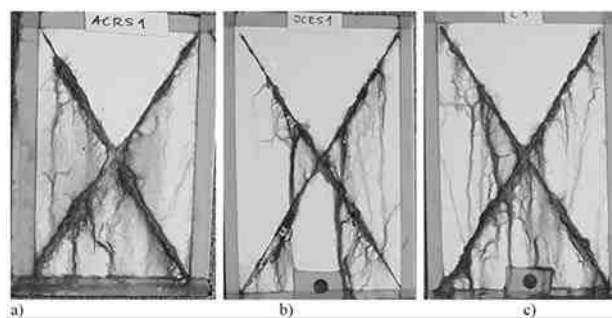

Figure 9—Salt spray test results of CRS panels after 1250 hr: (a) old epoxy-acrylate, (b) new epoxy-acrylate and (c) automotive reference.
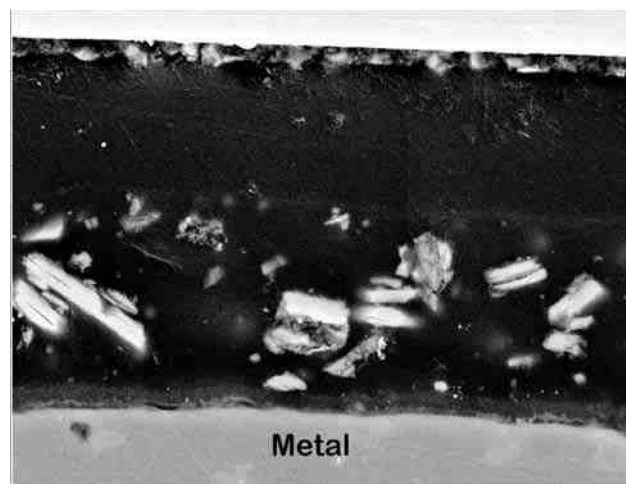

Figure 10—The SEM cross-section of the epoxy-acrylate coating on the metal after 30 days of salt immersion testing..
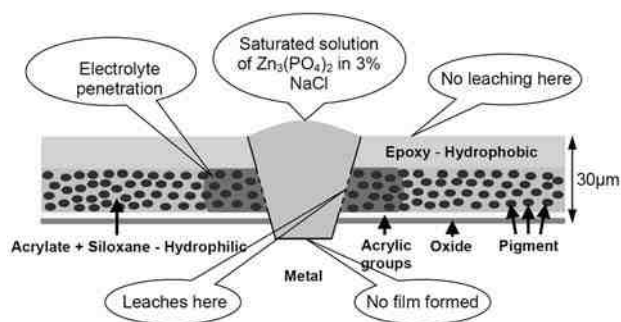
Figure 11—Principle of the corrosion inhibiting mechanism of the acrylate-epoxy-silane superprimer containing the zinc phosphate pigments, which protect the metal on-demand.

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 comparably to 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 with respect to the blistering tendency, then it will be a competitive candidate in challenging 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.

References

1. H.P. Rink & B. Mayer, *Progress in Organic Coatings*, **34,** 175 (1998).
2. M. Mager, *et al., Macromol. Mater. Eng.,* **286,** 682 (2001).
3. W. Lenhard, U. Neumann & W. Collong, *Progress in Organic Coatings,* **32,** 127 (1997).
4. G.P. Sundararajan, "Silane-Based Pretreatments of Electrocoated Metals for Corrosion Protection," MS Thesis, University of Cincinnati, Chemical and Materials Engineering, 2000.
5. T.F. Child & W.J. Van Ooij, *Chemtech.,* 2**8,** 26 (1998).
6. W.J. Van Ooij, *et al., Tsinghua Sci. Technol.,* **10,** 639 (2005).
7. A. Franquet, et al., Thin Solid Films, 348, 37 (2001).
8. M.F. Montemor, *et al., Progress in Organic Coatings,* **38,** 17 (2002).
9. C. Shivane, N.B.V. Simhadri & W.J. Van Ooij, *Proc. Fifth International Symposium on Silanes and Other Coupling Agents Conference, Toronto, Canada* (June 22-24, 2005).
10. C. Shivane, P. Puomi & W.J. Van Ooij, P*roc. Eurocorr 2006 Conference,* paper published on a conference CD, Maastricht, The Netherlands (Sept. 24-28, 2006).
11. *Ford Laboratory Test Method, BI-23-1,* April 30, 1981.
12. A. Seth, *et al., Progress in Organic Coatings,* **58,** 136 (2007).
13. A. Seth, "A Novel, One-Step, Low-VOC Primer for the Corrosion Protection of Aerospace Alloys and Metals," Ph.D. Thesis, University of Cincinnati, Chemical and Materials Engineering, 2006.

About the Author

Dr. Wim J. Van Ooij is a Professor in the Department of Materials Science and Engineering at the University of Cincinnati, Cincinnati, Ohio. He received his M.S. in Chemical Engineering in 1964 and his Ph.D. in Physical Chemistry in 1971 from Delft University of Technology in The Netherlands, both with highest honors. His prior affiliations have been (most recent first) as Senior Staff Scientist at Armco Research & Technology, Middletown, Ohio; Professor, Department of Chemistry, Colorado School of Mines, Golden, CO; Visiting Professor, Dept. of Materials Engineering, Virginia Tech, Blacksburg, VA; Senior Research Chemist, Akzo Research Laboratories, Arnhem, The Netherlands; Postdoctoral Associate, Ames Laboratory at Iowa State University and Sr. Research Associate, Delft University of Technology, Interuniversity Reactor Institute. He has been the recipient of many awards and honors over the years. His fields of special interest include: corrosion control of metals by organic coatings, secondary ion mass spectrometry, the chemistry of silanes at metal surfaces, electrochemical impedance spectroscopy, surface analysis of materials and plasma-polymerized coatings. He is a member of the American Chemical Society, the Materials Research Society, the China Ordnance Research Society, the Adhesion Society and the Royal Dutch Chemical Society.