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Corrosion Protection of Automotive Steels by Novel Water-borne Primer Systems

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Corrosion protection of automotive steels has traditionally been assured by using a zinc phosphate metal pretreatment followed by the deposition of a cathodic electrocoat system. This system has been developed and optimized over the years into a highly robust and dependable system with a high performance. However, in terms of efficiency and use of resources and energy, the need is now felt to develop a simpler system with fewer steps, shorter lines, less energy requirements (curing and e-coat deposition) and less stringent waste disposal requirement (phosphate sludge). We report here on the development of a one-step system that can possibly replace both the zinc phosphate and the e-coating processes. Such a system is based on the so-called superprimer concept that we have recently developed for the replacement of chromate pretreatment and chromate-containing primers in the aerospace industry. With some modifications, such systems can also be adapted for use in the automotive industry.

***Keywords**: automotive, steel, superprimer, chromate free, low-VOC.*

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 until the e-coating 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 rise and the lead present in the e-coating process. We have earlier proposed a silane-based replacement for the zinc phosphating pretreatment in the automotive finishing line.[1] It is well-known that silane-based treatments are environmentally attractive and are also much simpler than the phosphating process. They comprise of only three steps: alkaline cleaning, rinsing and silane dip or spray.[2-5] 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 primer and top-coated in the automotive finishing line.[6] The passivation treatment has been studied separately[6] and with an e-coat.[7] 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. Two versions of this primer were compared with a commercially available automotive coating system containing a trication pretreatment, an electrocoat and a typical automotive coating finish.

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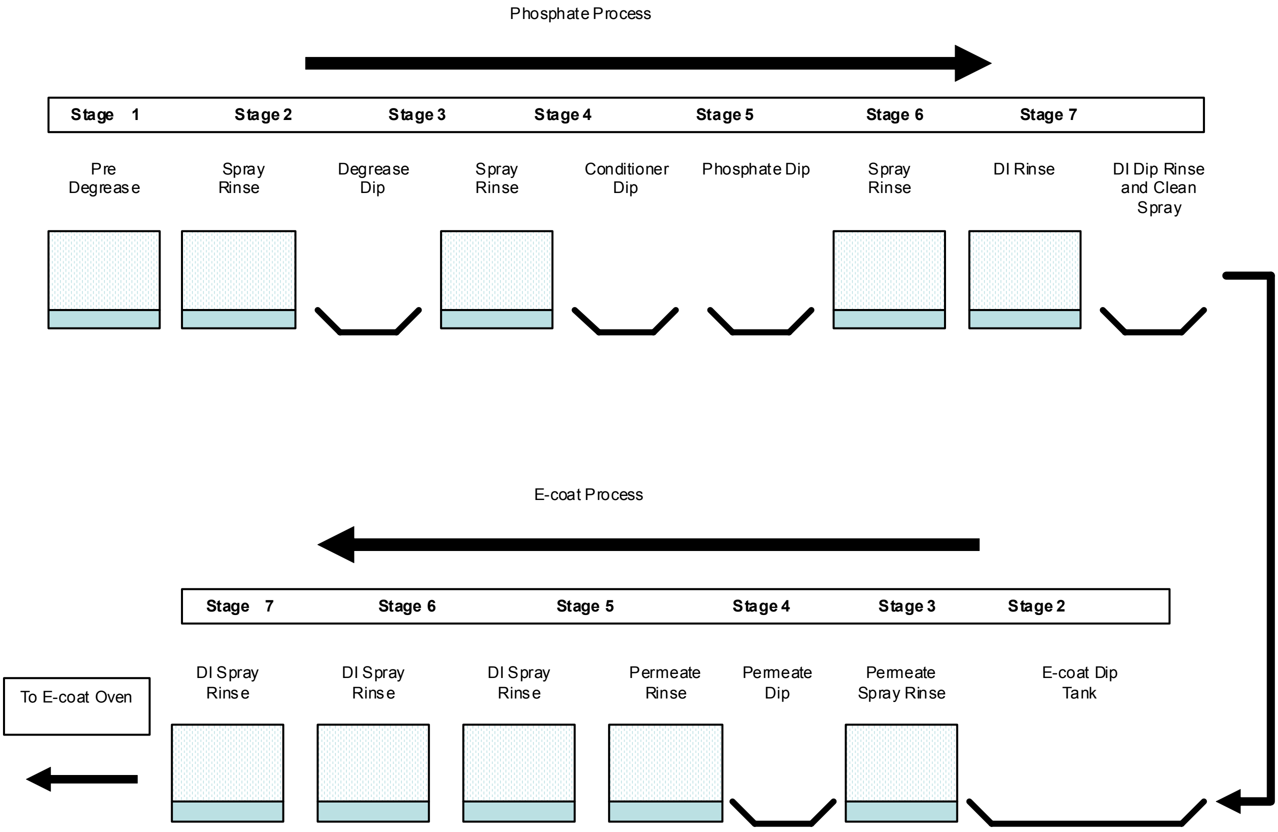


Fig. 1. The pretreatment and e-coating steps of a typical finishing line in the automotive industry.

2. Experimental

2.1 Substrate

Cold-rolled steel (CRS) from ACT Laboratories, Midland, Michigan was used in this study.

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 ECO-CRYL^{TM} 9790 acrylic resin and EPI-REZ^{TM} WD-510 epoxy. Both resins were from Hexion Specialty Chemicals, Houston TX. The second version is based on Maincote^{TM} AE-58 acrylic resin and Daubond 9010W55 epoxy. The

former was from Rohm & Haas, Philadelphia, PA and the latter from Daubert Chemical Company, Chicago, IL. Both primers contain 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 CRS panels were thoroughly degreased, 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-polyeser 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 CRS 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 ~ 2 mils	

2.3 Characterization and Testing

The epoxy-acrylate primer coating itself has been characterized extensively with various sophisticated tools and the mechanism by which it protects a metal has been reported elsewhere.[8)] Here we mainly report on the performance results of the epoxy-acrylate primer in the described automotive coating. 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 for 2 months with bare cut edges
- ASTM D-714 3.5 wt.-% NaCl solution immersion test for 7 weeks
- FORD AGPE test for 38 cycles
- ASTM B-117 salt spray test for 1250 hours

The Ford AGPE test 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℃.[9)] 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.

3. Results and Discussion

All three types of samples had excellent dry and wet adhesion, even after the extended immersion time of 10 days. The water immersion test with bare cute edges we usually do as a crude test in order to investigate, if the pigment in the primer has any leach out on-demand effect such as the chromate pigments have. This test is usually more suitable for galvanized steels, where the steel will be exposed only when the edges are cut bare. All three CRS samples showed, however, red rust bleeding from the bare cut edges already after about 12 hours of water immersion, i.e., the red rust bleeding from CRS is too heavy to be suppressed by a pigment in the primer. The test was continued for 2 months in order to monitor would there be significant differences in the samples after prolonged exposure to water. The superprimed panels did not show any blistering and the amount of red rust bleeding from the samples was similar in magnitude. Thus, this test and the adhesion test were not

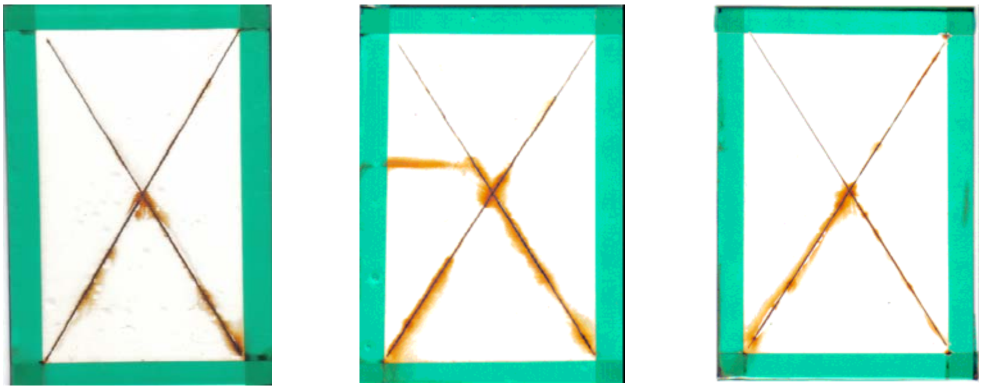

(a) (b) (c)

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

(a) (b) (c)

Fig. 3. Ford test results of CRS panels after 38 cycles; a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference.

able to differentiate between the performances of the samples. The ASTM D-714 salt water immersion test was able o show small differences in the performance of the stamples after 7 weeks. The results of this test are shown in Fig. 2.

According to Fig. 2 the first epoxy-acrylate and the reference panel are very similar when it comes to the extent of red rust in the scribe. The scribes of the second epoxy-acrylate seem slightly worse, but the surface appearance of the coating was slightly better on this sample than on the first epoxy-acrylate, which showed slight blistering in the coating. The salt water immersion test we use as a quick screening method to initially differentiate the performance of experimental coatings before we expose them to further testing. After this test the panels were exposed to the Ford AGPE test for 38 cycles. The panel images after the Ford test are shown in Fig. 3.

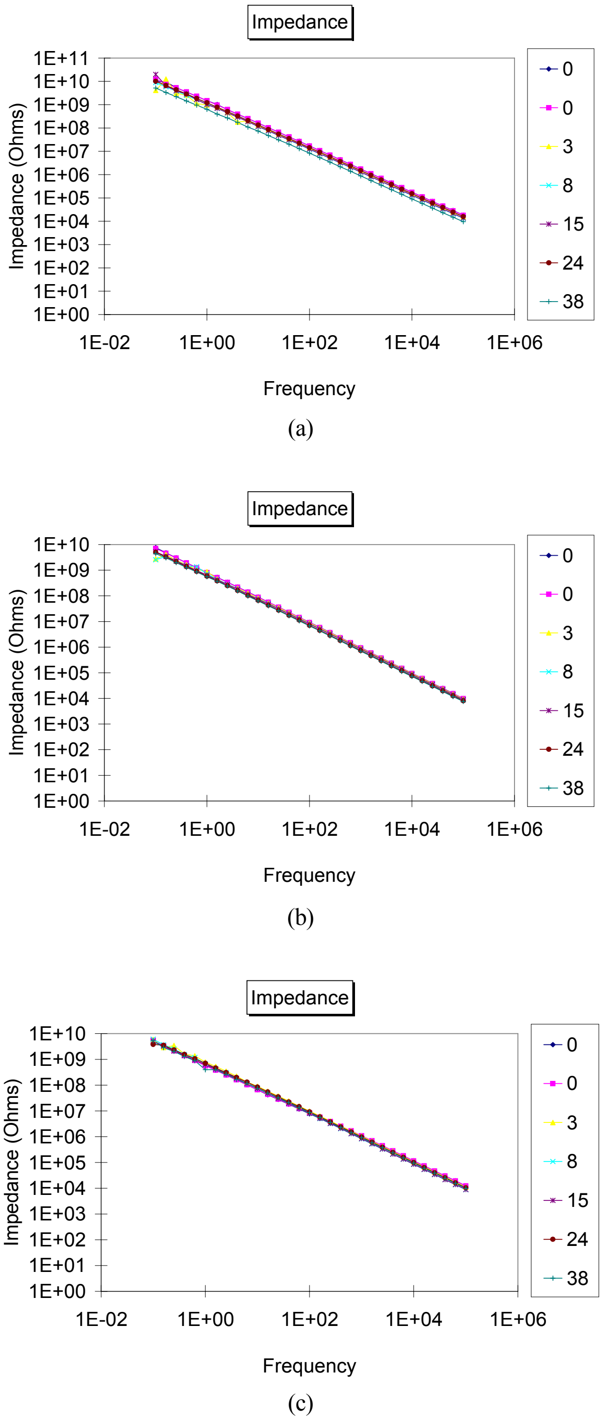
The replica panels had very similar performance in the Ford test. The scans chosen for Fig. 3 represent the performance of each sample. As can be seen from Fig. 3, the scribes of the second epoxy-acrylate were slightly better than for the two other panels and the surface of the second epoxy-acrylate sample was also better than for the first. In Fig. 3b slight blistering very close to the scribe can, however, be detected. It seems that when salt water or humidity is able to come in contact with the second epoxy-acrylate superprimer underneath the automotive coating, it is prone to blistering. 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 three samples are shown in Figs. 4 and 5, respectively.

As can be seen from Figs. 4 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 panel that deteriorates due to the corrosion reactions of the steel, which is exposed to the aggressive environments of the test through the cut.

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. Figs. 5 a) to c) show, however, that there is no change in the phase angle curves of the samples during exposure to the Ford test. The phase angle remains high between 80° to 90° throughout the frequency range on all samples. 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 panels after 1250 hrs of salt spray testing are shown in Fig. 6.

Fig. 6 shows a similar trend as the Ford results in Fig. 3; the scribe of the second epoxy-acrylate sample looks slightly better than for the two other samples. Fig. 6b) shows, however, again slight beginning of 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. 6) is quite different from the red rust formation in the Ford test (Fig. 3). 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

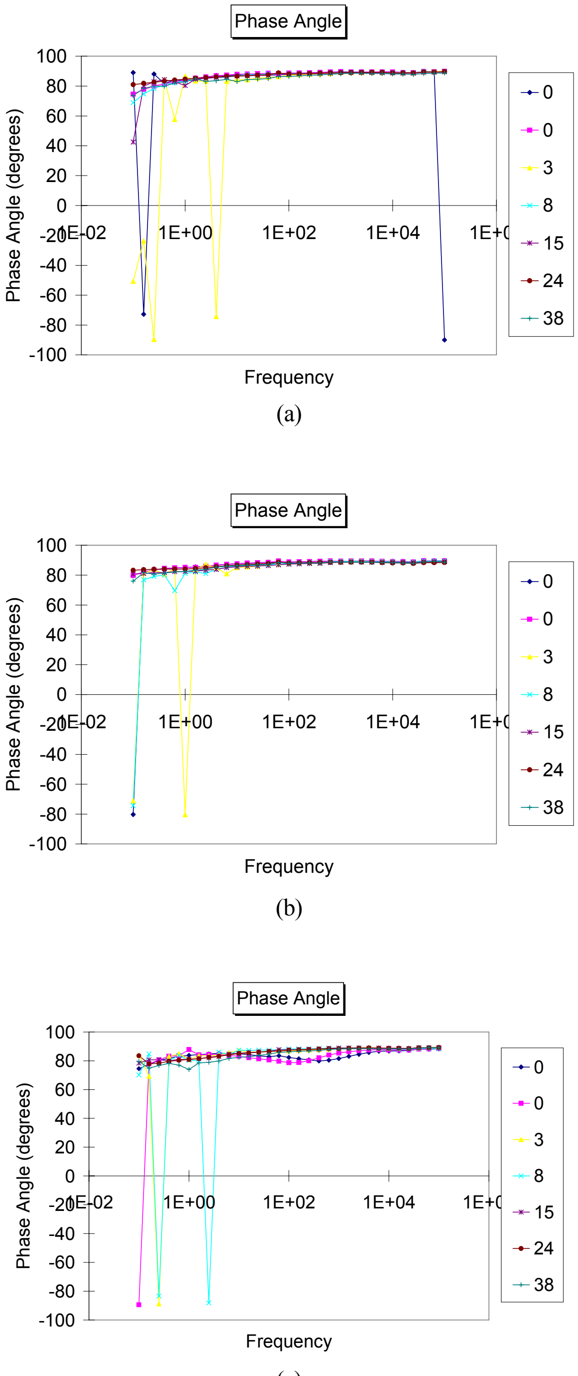


(a)

(b)

(c)

Fig. 4. The impedance as a function of frequency for the a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference.



(a)

(b)

(c)

Fig. 5. The phase angle as a function of frequency for the a) first epoxy-acrylate, b) second epoxy-acrylate and c) automotive reference.

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

(a) (b) (c)

Fig. 6. Salt spray test results of CRS panels after 1250 hours a) old epoxy-acrylate, b) new epoxy-acrylate and c) automotive reference.

slightly suppress further red rust formation in that particular spot.

As the scans in Figs. 2 and 6 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).

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. The wet adhesion of the superprimed panels was excellent and the corrosion resistance is comparable with the conventional technology. Overall the second epoxy-acrylate showed better performance than the first. When in contact with salty water through a scribe the second epoxy-acrylate is slightly prone to blister the automotive topcoat finish. If the primer can be improved in this respect, it will really be a competitive candidate in challenging the conventional 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 car.

Acknowledgments

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