PERFORMANCE OF CONDUCTIVE PRE-PRIMERS APPLIED ON GALVANIZED STEEL SHEETS FOR AUTOMOTIVE BODIES

D. Santos(1), H. Raminhos(1), M. Costa(1), T. Diamantino(1) and F. Goodwin(2)

ABSTRACT

The main driving forces concerning the use of pre-primed automotive sheet are corrosion protection increase and cost reduction during vehicle manufacturing. In this work, the behaviour of two conductive primers, codified by 1 and 2, was studied and compared with that of a conventional electrophoretic primer. Primer 1 is an organic zinc rich silicate with a low thickness (near 4 µm) and primer 2 is a very thin (near 2 µm) water based primer filled with graphite. These primers were applied on electrogalvanized, hot dip galvanized and galvannealed steel sheets.

Formability capabilities of pre-primed galvanized steel sheets were evaluated, through cupping and stone chipping tests, according to EN ISO 1520 and ASTM D3170, respectively. To evaluate corrosion protection, the samples were submitted to a corrosion cyclic test according to VDA procedure 621-415 contained in the SEP 1160. Corrosion mechanisms were studied by scanning electron microscopy (SEM) with X-ray microanalysis by dispersive energy spectrometry (EDS) associated.

Primers 1 and 2 offer cathodic protection when exposed, however by different manners, and allow previous welding works. Primer 1 acts as a zinc rich primer and primer 2 acts as a sealer of metallic zinc coatings, not allowing zinc depletion and delaying the appearance of iron corrosion from the steel substrate. After some exposure time it was possible to see on the surface of the primer 2, zinc corrosion products arising from the pores of the paint coating. Primers 1 and 2 applied with a low thickness, seem to be good alternatives to the conventional electrophoretic primers.

Key Words: Automotive, Conductive Pre-Primers, Steel Sheets, Metallic Zinc Coatings

1. INTRODUCTION

In the 1960's automotive body corrosion resulting from de-icing salt, used in winter in the heavy snowfall regions of North America and Northern Europe, became a serious economic problem. The Canadian government issued anti-corrosion standards for automobiles in 1976 [1], and automobile manufacturers later started providing anti-corrosion guarantees on the automobiles. In recent years, European and some other automobile manufacturers began offering 12-years warranties. Coatings are used to enhance appearance and assure that functional requirements are met. Electrocoat is a widely used coating technology that has provided excellent levels of performance on industrial metal materials for more than 40 years.
In the early 1960’s, anodic automobile body primers were commercialized. In 1971, cathodic technology was introduced, and in 1976 cathodic primers for automobiles appeared [2]. Several driving forces have increased the use of pre-primed automotive sheet in recent years [3]. High performance and cost reduction during vehicle manufacturing are the main requirements. It will be possible to save costs significantly if the conventional electrophoretic primer can be eliminated or its usage reduced. Introduction of conductive pre-primers in the automotive industry is a significant improvement because they are applied with low thicknesses and enable weldability. Corrosion resistance, forming, welding and adhesive bonding properties are important factors. In this work, the performance of two conductive primers were studied and compared with that of a conventional electrophoretic primer. These primers were applied on zinc coated steel sheets. Three zinc coatings were included: electrogalvanized (pure zinc), hot-dip galvanized and galvanneal.

2. EXPERIMENTAL

2.1 Materials

Substrates

Three metallic zinc coatings applied on steel, were used as substrates: Zn electrogalvanized, hot-dip galvanized and galvanneal, codified by EG, GI and GA respectively.

Primers

This study included: two different conductive primers (with different conductive fillers), codified by 1 and 2, and a conventional electrophoretically applied primer system used as baseline, codified by ELPO. Primer 1 was Grancoat ZE, a zinc based conductive primer, applied in the USA. Primer 2 was Grancoat X, a very thin conductive experimental primer containing graphite, applied in Germany. Previously to the application a primer, all the panels were pre-treated with a new environment-friendly (non-chrome) treatment, codified by Bonderite 1456X.

Panels with two shapes were considered: flat panels and "pie pan" deformed panels.

2.2 Studies

Thickness

The thickness of pre-primed samples was evaluated by two different methods: following the method 6A included in the ISO 2808 standard [4] and by scanning electron microscopy (SEM).

Total thickness of primers plus corresponding substrate was measured [4] using an Elcometer 200SP equipment. After that, the primer was removed by pickling and the thickness of the substrates was measured, being the thickness of the primer evaluated by subtraction to the total thickness.

Samples obtained by cross-section of pre-primed flat panels, were observed by SEM and the thickness of substrates and primers was evaluated. A high resolution Philips XL 30 FEG/EDAX NX scanning electron microscope was used.

Formability Capabilities

Cupping test

The cupping test was performed according to EN ISO 1520 [5]. Three of each sort of panels (EG, GI and GA), with primers were deformed using the equipment Erichsen model 202. After the panel was firmly fixed in the cupping apparatus (~10 kN), the test was carried out using a mean speed of indentation of about 4.3 mm m⁻¹. The test stopped immediately before fracture appeared, in others until a crack was first observed on the surface of the coating [5].

Stone chipping test

The stone chipping test was carried out, according to ASTM D3170 [6], in which three panels of each sort of panels (EG, GI and GA), with primers, were tested.

The panels were chilled to 0 °C before the test itself. The test lasted for about 15 seconds, using about 550 mL of gravel, with a maximum projection pressure of about 55 psi.

Corrosion Mechanisms

Cyclic corrosion test

The pre-primed samples were submitted to a corrosion cycle test according to the VDA-procedure 621-415 [7] contained in the SEP 1160 [8]. The cycle consists of:

- 1 day salt spray test according to DIN 50021-SS (ASTM B117) [9].
- 4 days cyclic humidity, being each daily cycle composed by 3 h at 40 °C and 98% relative humidity and 16 h at 23 °C and 50% relative humidity.
- 2 days ambient climate according to DIN 50014 [10].

Alternatively, the primer 1 was also exposed to a cycle according to SAE J2334 procedure [11], composed by:

In normal working days (during the week):
- 6 hours at 50 °C and 100% relative humidity.
- 5 minutes of salt spray (ASTM B117) [9].
- 17h 45 min at 60 ºC and 50% relative humidity.

In the weekends and holidays:
- always 60 ºC and 50% of relative humidity.

For salt spray and humidity exposures the Erichsen 606 and Tabai PR-25SP test chambers were respectively used.

Panels submitted to cupping test, panels submitted to stone chipping test and "pie pan" deformed panels were exposed.

Evaluation of corrosion severity

During and after cyclic corrosion tests, visual inspections were performed. Blisters found on samples submitted to stone chipping test were classified in accordance with EN ISO 4628 Standard part 2 [12].

Study of corrosion mechanisms by scanning electron microscopy (SEM)

With the purpose of knowing the corrosion mechanisms, samples were studied by scanning electron microscopy (SEM) with X-ray microanalysis by energy dispersive spectrometry (EDS) associated. This study included unexposed and exposed
samples. The surface and samples obtained by cross-section were studied. A high resolution Philips XL 30 FEG/EDAX NX scanning electron microscope was used. Before SEM/EDS studies, the samples were coated with a thin gold film.

3. RESULTS AND DISCUSSION

Tables 1 to 3 contain the mean thickness values of metallic coatings and primers. For primer 1, the evaluation of primer thickness from SEM micrographs was not feasible, due to difficult observation of the interface between the primer and the resin used for the preparation of cross section samples (Fig. 1). For the electrophoretic primer, due to its difficult removal by pickling, the individual thickness was measured on SEM micrographs (Fig. 2 and 3).

![Fig. 1](image1.png)
![Fig. 2](image2.png)

**Fig. 1 – Appearance, observed by SEM, of samples obtained by cross section of primer 1 applied on electrogalvanized, hot dip galvanized and galvannealed substrates.**

**Fig. 2 – Appearance, observed by SEM, of samples obtained by cross section of primer 2 applied on electrogalvanized, hot dip galvanized and galvannealed substrates.**

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Mean Coating Thickness (µm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG + Primer 1</td>
<td>8</td>
</tr>
<tr>
<td>GI + Primer 1</td>
<td>11</td>
</tr>
<tr>
<td>GA + Primer 1</td>
<td>10</td>
</tr>
</tbody>
</table>

* From pickling and measurements according to ISO 2808, Method 6A.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Mean Coating Thickness (µm)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG + Primer 2</td>
<td>6</td>
</tr>
<tr>
<td>GI + Primer 2</td>
<td>10</td>
</tr>
<tr>
<td>GA + Primer 2</td>
<td>9</td>
</tr>
</tbody>
</table>

** From SEM micrographs of samples obtained by cross section (Fig. 2).

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Mean Coating Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 2808, Method 6A</td>
<td>SEM micrograph (Fg)</td>
</tr>
<tr>
<td>EG + ELPO</td>
<td>33</td>
</tr>
<tr>
<td>GI + ELPO 35</td>
<td>35</td>
</tr>
<tr>
<td>GA + ELPO</td>
<td>35</td>
</tr>
</tbody>
</table>

The results of cupping and stone chipping tests are presented in Tables 4 and 5. Primers 1 and 2 showed formability capabilities similar to that of the electrophoretic primer.

Concerning cupping test, the Erichsen indices (IE) are similar for the three primers and for the three substrates, with difference between mean values less then 2 mm. Only the hot dip galvanized steel coated with the primer 2, with higher depth of indentation, seems to present some better formability.
However, the minimum depth of indentation at which the coating cracks was high for all of them.

From the results of stone chipping test, it was verified that the three primers present better performance when applied on hot-dip galvanized steel than on electrogalvanized or galvannealed steel. Generally, it was verified similar performance of samples with electrophoretic primer and of samples with primer 2, which is somewhat higher than that of samples with primer 1 with higher number of chips. In spite of the considerable number of chips observed (100-150 [6]), it was verified, that for the three primers and for the three substrates, these chips had small size (diameter: 1-3 mm [6]) and by SEM/EDS studies performed that they did not reach the steel substrate.

The results of visual inspections performed on the primers applied on the three substrates, with ‘pie pan’ and cupping deformations, submitted to 10 corrosion cycles according to the VDA-procedure 621-415 [7] are presented in Tables 6 to 8. These tables have annexed the corresponding pictures. Results of samples with stone chipping damage, submitted to cyclic corrosion test are presented in the some way in the Tables 9 to 11.

### Table 4
Results of Cupping Test

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>IE (mm)</th>
<th>Primer 1</th>
<th>Primer 2</th>
<th>ELPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG + Primer</td>
<td>9.5</td>
<td>10.0</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>GI + Primer</td>
<td>9.8</td>
<td>11.7</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>GA + Primer</td>
<td>9.5</td>
<td>9.8</td>
<td>9.8</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5
Results of Stone Chipping Test

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>No. of chips</th>
<th>Size of chips (mm)</th>
<th>No. of chips</th>
<th>Size of chips (mm)</th>
<th>No. of chips</th>
<th>Size of chips (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG + Primer</td>
<td>131</td>
<td>1-3</td>
<td>124</td>
<td>1-3</td>
<td>115</td>
<td>1-3</td>
</tr>
<tr>
<td>GI + Primer</td>
<td>125</td>
<td>1-3</td>
<td>106</td>
<td>1-3</td>
<td>102</td>
<td>1-3</td>
</tr>
<tr>
<td>GA + Primer</td>
<td>145</td>
<td>1-3</td>
<td>117</td>
<td>1-3</td>
<td>110</td>
<td>1-3</td>
</tr>
</tbody>
</table>

### Table 6
Results of exposure to 10 corrosion cycles according to the VDA-procedure 621-415 [7], of primer 1 submitted to cupping and “pie pan” deformations

<table>
<thead>
<tr>
<th>Area</th>
<th>EG + Primer 1</th>
<th>GI + Primer 1</th>
<th>GA + Primer 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>General overview</td>
<td>Considerable Zn corrosion</td>
<td>Considerable Zn corrosion</td>
<td>Moderate Zn corrosion</td>
</tr>
<tr>
<td>Pie pan</td>
<td>Considerable Zn corrosion</td>
<td>Considerable Zn corrosion</td>
<td>Moderate Zn corrosion</td>
</tr>
<tr>
<td>Cupping area</td>
<td>Zn corrosion with dripping; considerable Fe corrosion</td>
<td>Zn corrosion with dripping; slight to moderate Fe corrosion</td>
<td>Zn corrosion with dripping; slight to moderate Fe corrosion</td>
</tr>
</tbody>
</table>

### Table 7
Results of exposure to 10 corrosion cycles according to the VDA-procedure 621-415 [7], of primer 2 submitted to “pie pan” and cupping deformations

<table>
<thead>
<tr>
<th>Area</th>
<th>EG + Primer 2</th>
<th>GI + Primer 2</th>
<th>GA + Primer 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>General overview</td>
<td>Considerable Zn corrosion</td>
<td>Slight Zn corrosion; considerable Fe corrosion</td>
<td>Zn corrosion products; slight to moderate Fe corrosion</td>
</tr>
<tr>
<td>Pie pan</td>
<td>Considerable Zn corrosion; Fe corrosion in the Zn spots</td>
<td>Slight to moderate Zn corrosion</td>
<td>Moderate Zn corrosion</td>
</tr>
<tr>
<td>Cupping area</td>
<td>Considerable Zn corrosion; severe Fe corrosion</td>
<td>Considerable Zn corrosion; considerable Fe corrosion</td>
<td>Zn corrosion</td>
</tr>
</tbody>
</table>

### Table 8
Results of exposure to 10 corrosion cycles according to the VDA-procedure 621-415 [7], of electrophoretic primer submitted to cupping and “pie pan” deformations

<table>
<thead>
<tr>
<th>Area</th>
<th>EG + ELPO</th>
<th>GI + ELPO</th>
<th>GA + ELPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>General overview</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>Pie pan</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td>Cupping area</td>
<td>Moderate Zn corrosion in the rupture area; moderate Fe corrosion; blisters 4(S3)</td>
<td>Considerable Zn corrosion in the rupture area; slight Fe corrosion</td>
<td>Slight Zn corrosion in the rupture area; considerable Fe corrosion; blisters 4(S3)</td>
</tr>
</tbody>
</table>
Iron corrosion was not observed on the surface without damage, of the three primers applied on the three substrates. More or less zinc corrosion appeared on the surface of primers 1 and 2. Primer 1 is a zinc rich primer (Fig. 4), and after cyclic corrosion test by SEM, on its surface acicular aggregates and plate-like hexagonal crystals were observed (Fig. 5). Chloride was detected by EDS mainly on the plate-like hexagonal crystals. X-ray diffraction (XRD) studies previously performed on zinc rich primers exposed in salt spray cabinet [13] showed that this crystal correspond to the trigonal compound $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot2\text{H}_2\text{O}$. In these studies previously performed, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ was identified by XRD as the major component of acicular aggregates in agreement with the results of van Eijnsbergen [14] and others [15]. Hydroxyl chloride, $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot2\text{H}_2\text{O}$, can also be present in acicular aggregates.

The first step in zinc surface degradation seems to be oxidation followed by hydration and fast carbonation as already outlined by several authors [13–14, 16]. In the salt spray cabinet, humidity, temperature and chloride concentration could help to replace basic zinc carbonate and other zinc compounds by increasingly dense plate-like structures of basic zinc chloride (pseudo-hexagonal crystals). X-ray diffraction (XRD) studies previously performed on zinc rich primers exposed in salt spray cabinet [13] showed that this crystal correspond to the trigonal compound $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot2\text{H}_2\text{O}$. In these studies previously performed, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ was identified by XRD as the major component of acicular aggregates in agreement with the results of van Eijnsbergen [14] and others [15]. Hydroxyl chloride, $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot2\text{H}_2\text{O}$, can also be present in acicular aggregates.

Table 9
Results of exposure to 10 corrosion cycles according to the VDA-procedure 621-415 [7], of primer 1 submitted to stone chipping test

<table>
<thead>
<tr>
<th>Area</th>
<th>EG + Primer 1</th>
<th>GL + Primer 1</th>
<th>GA + Primer 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>General overview</td>
<td>Moderate to considerable Zn corrosion</td>
<td>Moderate Zn corrosion</td>
<td>Slight Zn corrosion</td>
</tr>
<tr>
<td>Stone chipping area</td>
<td>Slight Zn corrosion; slight Fe corrosion</td>
<td>Severe Zn corrosion; slight Fe corrosion</td>
<td>Slight Zn corrosion; slight Fe corrosion</td>
</tr>
</tbody>
</table>

Table 10
Results of exposure to 10 corrosion cycles according to the VDA-procedure 621-415 [7], of primer 2 submitted to stone chipping test

<table>
<thead>
<tr>
<th>Area</th>
<th>EG + Primer 2</th>
<th>GL + Primer 2</th>
<th>GA + Primer 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>General overview</td>
<td>Slight Zn corrosion</td>
<td>Slight Zn corrosion</td>
<td>Slight Zn corrosion</td>
</tr>
<tr>
<td>Stone chipping area</td>
<td>Moderate Zn corrosion; slight Fe corrosion</td>
<td>Moderate Zn corrosion; slight Fe corrosion</td>
<td>Slight Zn corrosion; slight Fe corrosion</td>
</tr>
</tbody>
</table>

Iron corrosion was not observed on the surface without damage, of the three primers applied on the three substrates. More or less zinc corrosion appeared on the surface of primers 1 and 2. Primer 1 is a zinc rich primer (Fig. 4), and after cyclic corrosion test by SEM, on its surface acicular aggregates and plate-like hexagonal crystals were observed (Fig. 5). Chloride was detected by EDS mainly on the plate-like hexagonal crystals. X-ray diffraction (XRD) studies previously performed on zinc rich primers exposed in salt spray cabinet [13] showed that this crystal correspond to the trigonal compound $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot2\text{H}_2\text{O}$. In these studies previously performed, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ was identified by XRD as the major component of acicular aggregates in agreement with the results of van Eijnsbergen [14] and others [15]. Hydroxyl chloride, $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot2\text{H}_2\text{O}$, can also be present in acicular aggregates.
On the surface of unexposed primer 2, with a very low thickness, it was possible to detect, by EDS, the presence of zinc from the substrate (Fig. 6).

After a short exposure time, zinc corrosion products were visible, which arose through the pores of the coating, as acicular aggregates and plate-like hexagonal crystals (Figure 7).

Regarding the “pie pan deformation”, iron corrosion was only observed in the zinc spots of electrogalvanized steel coated with the primer 2.

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Regarding the “pie pan deformation”, iron corrosion was only observed in the zinc spots of electrogalvanized steel coated with the primer 2.
On the cupping area, more or less iron corrosion was observed in all primers and substrates. Electrophoretic primer presented lower performance, with significant blister formation.

Concerning the stone chipping area, the results obtained for the three primers are similar. However, electrogalvanized and hot-dip galvanized steels coated with primer 2 presented less iron corrosion than when coated with primer 1 and electrophoretic primer.

Among the three substrates, galvanneal seems to be the one that presented the best performance on the stone chipping area. Only slight iron corrosion was observed for the three primers. On the cupping area of samples coated with primer 1 and 2, the best and worst performance was presented by galvannealed steel and electrogalvanized steel, respectively.

4. CONCLUSIONS

Primers 1 and 2 showed formability capabilities similar to that of the electrophoretic primer. Concerning cupping test, the Erichsen indices (IE) are similar for the three primers and for the three substrates. On samples submitted to stone chipping test, it was, generally, verified similar performance of samples with electrophoretic primer and of samples with primer 2. Primer 1 presented somewhat lower performance.

For primers 1 and 2 applied on the three zinc substrates (electrogalvanized, galvannealed and hot-dip galvanized steel), after 10 corrosion cycles according to VDA procedure 621-415, the degradation on the undamaged surface and on the pie pan deformation was low, or not significant. Red corrosion was not observed on the undamaged surface. On pie pan deformation, iron corrosion appeared only for the primer 2 applied on electrogalvanized steel.

On cupping area the worst performance was presented by electrophoretic primer, with significant blisters formation.

Concerning the combination substrate/primer, on the cupping area, primers 1 and 2 presented the best and the worst performances when applied on galvannealed steel and electrogalvanized steel, respectively. On the stone chipping area, for all three primers, the best performance was observed when they had been applied on galvannealed steel. More iron corrosion was generally verified for the primers applied on electrogalvanized steel.

On the surface of primer 1 submitted to cyclic corrosion test, thin acicular crystals and plate-like hexagonal crystal were observed by SEM. Aggregates of acicular crystals can correspond to basic zinc carbonate \( \text{Zn}_2(\text{OH})_2(\text{CO}_3)_2 \) and plate-like hexagonal crystal to zinc hydroxychloride hydrate \( \text{Zn}_2(\text{OH})(\text{Cl})(\text{Cl}_2 \cdot \text{H}_2\text{O}) \). Humidity and temperatures conditions, and the relative polarizability of \( \text{OH}^- \), \( \text{CO}_3^{2-} \) and \( \text{Cl}^- \) ions, may be responsible for the mechanisms of formation of the different types of zinc corrosion products observed. Basic zinc carbonate and other zinc compounds can be replaced by increasingly dense plate-like structures of basic zinc chloride (pseudo-hexagonal crystals).

Primer 2 is a water-based primer with graphite filler and, due to its very low thickness (near 2 µm), before exposure zinc from the metallic coating substrate, was detected by EDS. After 5 cycles exposure, it was possible to see by SEM, zinc corrosion products on the surface of primer 2 arising from the pores of the paint coating, in the form of acicular aggregates and of plate-like hexagonal crystals. As in the case of primer 1, the major compound of acicular aggregates should be basic zinc carbonate (hidrozincite) and the plate-like hexagonal crystals can correspond to zinc hydroxychloride hydrate.

The primer 2, with a very low thickness, acts as a sealer of metallic zinc coatings, not allowing the zinc “exhaustion”, and delaying the appearance of iron corrosion from the steel substrate.

Primers 1 and 2 applied with low thickness, showed to be good alternatives to the conventional electrophoretic primer system. According to SEM studies, they offer cathodic protection when exposed, however by different manners, and added to this they allow previous welding works.

ACKNOWLEDGMENTS

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REFERENCES