

## Research Article

# Assessment of Automotive Coatings Used on Different Metallic Substrates

W. Bensalah,<sup>1</sup> N. Loukil,<sup>1</sup> M. De-Petris Wery,<sup>2</sup> and H. F. Ayedi<sup>1</sup>

<sup>1</sup> *Laboratoire de Génie des Matériaux et Environnement (LGME), ENIS, Université de Sfax, B.P.W. 1173-3038, Tunisia*

<sup>2</sup> *IUT Mesures Physiques d'Orsay, Université Paris Sud, Plateau du Moulon, 91400 Orsay, France*

Correspondence should be addressed to W. Bensalah; [walidbensalah@gmail.com](mailto:walidbensalah@gmail.com)

Received 12 January 2014; Revised 20 March 2014; Accepted 26 March 2014; Published 29 April 2014

Academic Editor: Sebastian Feliu

Copyright © 2014 W. Bensalah et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Four epoxy primers commonly used in the automotive industry were applied by gravity pneumatic spray gun over metallic substrates, specifically, steel, electrogalvanized steel, hot-dip galvanized steel, and aluminum. A two-component polyurethane resin was used as topcoat. To evaluate the performance of the different coating systems, the treated panels were submitted to mechanical testing using Persoz hardness, impact resistance, cupping, lattice method, and bending. Tribological properties of different coating systems were conducted using pin on disc machine. Immersion tests were carried out in 5% NaCl and immersion tests in 3% NaOH solutions. Results showed which of the coating systems is more suitable for each substrate in terms of mechanical, tribological, and anticorrosive performance.

## 1. Introduction

Painting a vehicle is one of the most expensive operations in automotive industry. The painting process typically involves 30–50% of an automotive assembly plant's costs [1]. This high cost is attributed to the need to have high quality coatings and the necessity of meeting strict environmental regulations. The coated surface must be finished in a way that provides an excellent surface quality [1, 2].

Automotive paint has two main functions [2, 3]: (i) to make the vehicle look good and (ii) to protect the underlying metal from the harsh environment to which it is exposed. A typical automotive paint system consists of many different layers, each chosen for a precise function: (i) clearcoat, expected to protect underlying layers and maintain a shiny appearance, (ii) basecoat, containing the visual properties of colors or chromophoric layer, (iii) primer, acting as leveler and as protector, and/or (iv) e-coat, to provide corrosion protection.

Despite the advances in surface coating technologies, priming remains the fundamental phase to prevent corrosion [3]. Protection against any form of corrosion and paint film durability is and will be of major importance.

The purpose of priming in the automotive industry is [1–4] (i) to inhibit corrosion of the metal substrate from discontinuities in the paint system which may occur during application, (ii) to resist mechanical damage to the paint system and to stop its propagation to the metal substrate, (iii) to provide adhesion to the substrate and to the subsequent multilayers system, and (iv) to contribute to the coating systems' aesthetic aspect by reducing surface roughness.

Many researchers have focused on the chemical-mechanical priming performances. Kumar and Nigam [5] have studied the effect of the corrosion of cold rolled mild steel beneath two types of epoxy primers after immersion for six months in 3% NaCl. They have found that the chemical composition of the formed rust depended on the nature of the anticorrosive pigment present in the primer coating. Lonyuk et al. [6] have investigated eight different coating systems containing different primers in terms of mechanical properties. They have observed failure by delamination between the topcoat and primer for some coating systems and adhesive failures between the primer and substrate for others. Other authors [7–10] have demonstrated the great effect of the substrate type on the degradation of the painted metal. Suay et al. [7] have shown that the best

performance properties of the primer were obtained when it was applied on phosphatized steel compared to the cold rolled steel. Miller [8] showed that the reactivity of a metal substrate and the type of corrosion product formed had an influence upon the reliability of a protective coating. Kittelberger and Elm [9] concluded, in their work, that the type of the substrate was responsible for paint blistering susceptibility. Walter [10] focused on paint coatings on steel, galvanized steel, Zn/55% Al coated steel, and aluminium immersed in 5% NaCl solution at 50°C. He concluded that the corrosion performance of these coatings, as measured by their delaminating time, was directly related to the corrosion resistance of the unpainted substrate.

The present work aims to characterize the mechanical, tribological, and corrosion behaviors of four commercial coating primers and a commercial topcoat applied on four different substrates (steel, hot-dip galvanized steel, electrogalvanized steel, and aluminium) in order to understand and thereby improve the durability of the final paint/metal system used in industry.

For the evaluation of coating systems performance, several tests have been used: mechanical testing using Persoz hardness, impact resistance, cupping, lattice method, and bending. Tribological properties of different coating systems were conducted using pin on disc machine. Immersion and electrochemical tests were carried out in 5% NaCl and 3% NaOH solutions.

## 2. Experimental

**2.1. Materials.** Two sets of painted panels representing commercial primer coated substrates and commercial topcoat/primer coated substrates were examined. Each set contained a series of 16 panels that had been painted with or without a topcoat. Four commercial anticorrosive epoxy primers, namely, PPG primer (PP), AMERLOCK primer (AP), STANDOX primer (SP), and DEBEER primer (DP), were applied on four types of substrates: steel, hot-dip galvanized steel, electrogalvanized steel, and aluminium. Primer types, substrates, and their mechanical properties are summarized in Tables 1, 2, and 3. The electrogalvanizing and hot-dip galvanizing of steel panels were carried out under industrial subcontracting. The hot-dip galvanizing process involves three steps prior to the immersion of the panels into the molten zinc bath (460°C): (i) caustic cleaning in a hot alkali solution to eliminate organic contaminants, (ii) pickling in a heated sulphuric acid solution, and (iii) fluxing of the steel panels by immersion into an aqueous solution of zinc ammonium chloride and then drying before zinc deposition. The thickness of the zinc coating is about 50  $\mu\text{m}$ . For the electrogalvanizing process, steel panels were mechanically polished, chemically decreased in commercial alkaline solution, and then etched in 20% HCl solution at room temperature. Water rinsing was used after each step. Afterwards, panels were electrogalvanized ( $J = 1.2 \text{ A dm}^{-2}$ ) in vigorously stirred acid bath DUZINC 019-LF from MAC-DERMID maintained within  $30 \pm 0.1^\circ\text{C}$ . The thickness of the zinc coating is about 20  $\mu\text{m}$ .

Primer coatings were applied using gravity pneumatic spray gun. Before application, viscosity and density of the different primers coatings were measured. The paint dry film thicknesses were maintained within the  $75 \pm 5 \mu\text{m}$  range and were controlled using an Elcometer 355 Top Thickness Gauge equipped with eddy current probe. The commercial topcoat was a two-component polyurethane resin with a thickness of  $75 \pm 5 \mu\text{m}$ .

### 2.2. Testing Methods and Equipment

**2.2.1. Persoz Pendulum Hardness Test (ASTM D 4366-95).** The instrument consisted of a pendulum which was free to swing on two steel balls resting on a coated test panel. The pendulum hardness test was based on the principle that the amplitude of the pendulum's oscillation would decrease more quickly when supported by a softer surface.

The stainless steel balls, 8 mm diameter, were of hardness HRC59. The total weight of the pendulum was 500 g. The period of oscillation was 1 sec and the time for damping from a 12-degree displacement to 4-degree displacement was taken. Three tests were performed to each coated sample and the final result was the average of the three experiments.

**2.2.2. Impact Resistance Test.** Impact tests have been performed over coated samples by making the impact from the substrate side (reverse impact) according to ISO 6272.

The impact tests consisted of checking the primer damage resistance to the collision of a ball (1000 g) dropped from a fixed height of 0.5 m directly onto the metal substrate side and evaluating if the coating on the other side had been damaged or not. The weight was dropped through a guiding tube whose height was incrementally marked.

**2.2.3. Resistance of the Coating against Cupping in an Erichsen Cupping Test (ISO 1520).** The objective of this test was to identify the resistance of the paint film against the ongoing deformation of a coated substrate panel with a pressed-in 20 mm steel ball. The result of the test gives the so-called "cupping" in mm during which the first disturbance of the coating occurred.

**2.2.4. Degree of Coating Adhesion by a Lattice Method.** Determination was made by means of a special cutting blade with 6 cutting edges 2 mm apart and involved the degree of adhesion of the created 2 mm  $\times$  2 mm squares to a base substrate in accordance with standard ISO 2409.

**2.2.5. Coating Resistance during Bending on a Cylindrical Mandrel.** This identified the resistance of the paint film against ongoing deformation of a coated substrate panel around a 2 cm diameter stainless steel mandrel, verifying the disruption of paint film cohesion during the bending of the painted substrate panel (ISO 1519).

**2.2.6. Friction Test.** Friction tests were carried out in dry conditions using a pin-on-disc tribometer. Coated samples

TABLE 1: Chemical composition of the used substrates.

(a) Steel									
Element	C	P	S	N	Fe				
Weight (%)	≤0.18	≤0.05	≤0.05	≤0.009	Rest				
(b) Steel for hot-dip galvanizing									
Element	C	Mn	P	S	Fe				
Weight (%)	≤0.17	≤1.4	≤0.045	≤0.045	Rest				
(c) Steel for electrogalvanizing									
Element	C	Si	Mn	P	S	Al	N <sub>2</sub>	Fe	
Weight (%)	≤0.041	≤0.009	≤0.28	≤0.007	≤0.008	≤0.030	≤0.0034	Rest	
(d) Aluminum (Al5754H111)									
Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
Weight (%)	<0.40	<0.40	<0.10	<0.50	2.6–3.6	<0.30	<0.20	<0.15	Rest

TABLE 2: Mechanical properties of the used substrates

	Maximum stress		Yield stress		Elongation $A_{\min}$ (%)
	$R_m$ (MPa)		$R_{p0.2}$ (MPa)		
	Min	Max	Min		
Steel	370	450	240		25
Steel for hot-dip galvanization	360	510	235		24
Steel for electrogalvanization	340	470	235		26
Aluminum	190	240	80		18

with dimensions of  $20 \times 20 \times 3 \text{ mm}^3$  were brought into contact with 100Cr6 steel ball with a diameter of 6 mm. All tests were performed at the same sliding speed of 100 tr/min (0.052 m/s). The applied normal load was 1 N.

Friction tests were performed in ambient air (25–27°C) at 35–45% relative humidity (RH). During tests, the variation of the friction coefficient versus time was recorded.

**2.2.7. Corrosion Test.** The corrosion test applied to the coated substrates consisted only of samples after immersion into two solutions 3% NaOH and 5% NaCl at 25°C. A circular scratch surface ( $1 \text{ cm}^2$ ) was made through the coating with a sharp instrument so as to expose the underlying metal to the aggressive environment. The panels were evaluated to assess failure at the scratch mark. Evaluation of specimens was performed after different exposure times (2, 7, and 15 days) and consisted in the measurement of scratched surface increase.

**2.2.8. Electrochemical Tests.** Potentiodynamic polarization tests of the coated samples were conducted with a conventional three-electrode cell and an Autolab PGSTAT302N controlled by NOVA software allowing data acquisition. Platinum sheet was used as a counter electrode and saturated calomel electrode (SCE) as a reference one. The tested coated samples were firstly allowed to reach a steady open circuit potential (OCP). Both OCP and polarization tests were

carried out at room temperature (23°C) with a constant scanning rate of 5 mV/s under stirred conditions (300 rpm).

**2.2.9. Surface Morphology.** Surface profiles, using Surtronic 25 profiler from Taylor Hobson, were used to examine the surface topography of different paint coatings. The morphology of the corroded and delaminated paint coatings was studied using a LEICA optical microscope.

### 3. Results and Discussion

#### 3.1. Mechanical and Tribological Behaviors

**3.1.1. Persoz Pendulum Hardness Test (ASTM D 4366-95).** The Persoz hardness of the retained primers and primers/topcoat applied on the different substrates was measured. Knowing that standards require a Persoz hardness of the primers greater than 120 s, the surface hardness of both primers and primers/topcoat was around 120–140 s. In general, the hardness of a polymeric coating is an excellent probe of its chain stiffness [11]. For this reason, all coatings seem to have high adhesion on the painted panels.

**3.1.2. Impact Resistance Test.** The results of the impact resistance test of different primers and primers/topcoat are shown in Table 4. It is found that delamination occurs only with the aluminum panel for all primers and primers/topcoat used. From these impact resistance tests it can be concluded that

TABLE 3: Characteristics of different primers.

	PP	SP	DP	AP
Chemical base	Polyester-urethane chemistry	1K Primer filler	Polyaminoamide	AMERLOCK 400AL
Curing temperature	Ambient air	Ambient air	Ambient air	Ambient air
Curing duration	7 days	7 days	7 days	7 days
Color	Yellow	Gray	Gray	Gray
Glossiness	Mate	Mate	Mate	Semigloss

TABLE 4: Results of the impact resistance test of different primers and primer/topcoat systems.

	PP	SP	AP	DP
Aluminum panel	D	D	D	D
Steel panel	ND	ND	ND	ND
Hot-dip galvanized steel	ND	ND	ND	ND
Electrogalvanized steel	ND	ND	ND	ND
Primer/topcoat system				
Aluminum	D	D	D	D
Steel	ND	ND	ND	ND
Hot-dip galvanized steel	ND	ND	ND	ND
Electrogalvanized steel	ND	ND	ND	ND

ND: not delaminated; D: delaminated.

the delamination is practically independent of the “type” of paint system but is influenced by the substrate and especially by the large deformation of aluminum compared to the other substrates. It is to be noted that the presence of the zinc coating layer (hot-dip galvanized or electrogalvanized) has not shown a negative effect on the impact resistance of the painted systems.

**3.1.3. The Resistance of the Coating against Cupping.** During film formation and apart from the mechanism involved (evaporation of solvent, coalescence, chemical reaction, or their combination), in almost all cases the coating tends to contract. If this contraction is prevented by coating adhesion to its substrate and/or the mobility of macromolecular segments is hindered, a tensile stress will develop in the coating.

Standards require 4 mm as a minimum value of cupping for coating to be accepted. The cupping test is conducted with a relatively slow rate. The cupping action is stopped when cracking in the coating is visually detected.

As shown in Figure 1(a), the behaviors of PP and SP primers are conforming to the industrial regulations, for all substrates, whereas the other two primer coatings, AP and DP, are not. If nonmetallic coated steel and aluminum substrates with PP and SP primers have comparative behaviors, zinc coated steels (hot-dip galvanizing or electrogalvanizing) show considerable differences. The trend observed previously is not valid in the cases of AP and DP primers, for which the behavior is strongly influenced by substrate’s nature. Placing the primers in order from best to worst in terms of cupping, we obtain the sequence  $SP > PP > AP > DP$ .

The presence of the topcoat seems to enhance remarkably this property for primers PP, AP, and DP/topcoat systems,

whereas for a SP/topcoat system the cupping resistance is lower (Figure 1(b)).

**3.1.4. The Degree of the Adhesion of Coatings by a Lattice Method.** This method is an adequate means for controlling the level of adhesion strength after the coating has been spread and cured on the substrate. Moreover, it allows the detection of any failure in the case of the dissolution of the bond between coating and substrate.

After a lattice pattern is cut into the coating, the examination of the created grid area was conducted using an illuminated magnifier. This method is used for a quick pass/fail test. In the rather qualitative standardized tape-test the scales used to classify the specimens are from 0 to 5; that is, 0 corresponds to a very poor and 5 to a very good adhesion. Table 5 shows the lattice method results realized on the different primers and primers/topcoat. It is to be noted that class “0” indicates that the edges of the cuts are completely smooth; none of the squares of the lattice are detached and class “1” indicates the detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area, not significantly greater than 5%, is affected. All higher classes would then signal that something must be done to improve the coating’s adhesion. Table 5 shows good adhesion strength of the whole coating systems.

**3.1.5. The Resistance of the Coating during Bending on a Cylindrical Mandrel.** Automotive coating must have high flexibility and formability to overcome the harsh conditions such as cutting, pressing, and stamping process.

This test is often used for evaluating the flexibility of the coating. Although it is difficult to control the strain rate in this manually operated test, it can provide very useful flexibility ratings.

In Table 6 are shown the results of the bending test of different primers and primers/topcoat systems. PP and SP primers, with and without topcoating, were not cracked under bending tests for all substrates. For the DP primer, it seems that the topcoat improves the bending behavior of the coating system.

**3.1.6. Abrasion Resistance Test.** Abrasion resistance is a basic factor in the durability of the polymeric coating. Abrasion is caused by mechanical actions such as rubbing, scraping, or erosion from wind and water. It can take two general forms: marring or wearing. Abrasion resistance is related to physical characteristics such as hardness. The general agreement is that the major source of mar damage is a carwash, a normal

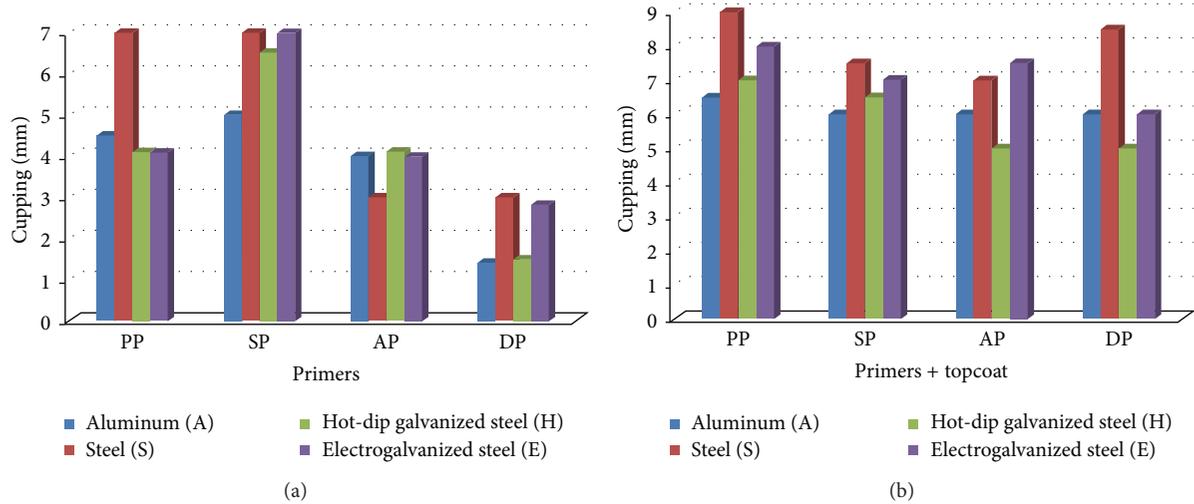


FIGURE 1: Results of the cupping in an Erichsen cupping tester: (a) primer; (b) primer/topcoat system.

TABLE 5: Results of the lattice method.

	PP	SP	AP	DP
Aluminum	0	0	0	0
Steel	0	1	0	0
Hot-dip galvanized steel	0	0	0	0
Electrogalvanized steel	0	1	0	0
Primer/topcoat system				
Aluminum	0	0	0	0
Steel	0	1	0	0
Hot-dip galvanized steel	0	1	0	0
Electrogalvanized steel	0	0	0	0

TABLE 6: Resistance of the coating during bending on a cylindrical mandrel.

	PP	SP	AP	DP
Aluminum	NC	NC	C	C
Steel	NC	NC	NC	NC
Hot-dip galvanized steel	NC	NC	NC	C
Electrogalvanized steel	NC	NC	NC	C
Primer/topcoat system				
Aluminum	NC	NC	C	C
Steel	NC	NC	NC	NC
Hot-dip galvanized steel	NC	NC	NC	NC
Electrogalvanized steel	NC	NC	NC	NC

C: cracked, NC: not cracked.

periodic activity for many automobile owners. During a car wash, dust embedded in the brush, and in some cases the brush itself causes numerous microscale scratches on the surface.

Prior to friction tests the roughness measurements, in terms of arithmetic roughness Ra, of the retained primers/topcoat systems were conducted (Figure 2). The obtained values were Ra = 0.172 μm, Ra = 0.129 μm, Ra = 0.100 μm, and Ra = 0.063 μm for AP, DP, PP, and SP/topcoat, respectively. These values show a very satisfactory surface morphology. In this section the friction coefficient of the retained primers/topcoat applied on aluminum is studied as a function of sliding time (Figure 3).

Before studying coatings, friction behaviour of the aluminium substrate was investigated. The evolution of the friction coefficient reveals three regions: friction first increases abruptly, then gradually increases, and finally achieves a steady state value for the rest of the sliding distance.

Turning to primer/topcoat systems, their friction coefficients show globally similar tendencies. The friction coefficients are stable at values between 0.3 and 0.4, and then they increase to values similar to that of the aluminium substrate indicating so the rupture of the coating system. For all coatings, there is adhesion at the beginning of the test

which suggests the formation of a junction over the area of real contact and the presence of shearing during sliding [12]; this phenomenon is more pronounced with the AP/topcoat system. Figure 3 indicates clearly that a fracture or rupture occurred for each of the coatings at a given transition point characterized by sharp increase in the friction coefficient. As it increases further, the magnitude of the rupture increases, eventually generating debris. According to Lin et al. the transition point corresponds to the deformation mechanism shifting from pure plastic deformation to plastic deformation with fracture or rupture [13].

One possible measure for mar and wear resistance is based on the appearance of the transition point. Based on this criterion the relative ranking of different coating from best to worst would be AP > SP > PP > DP.

3.2. Immersion and Electrochemical Tests. During the course of environmental exposure, water, oxygen, and salts diffuse through the paint system [14] causing substrate corrosion and inducing the precipitation of corrosion products between the paint system and metal. These products affect the adhesion

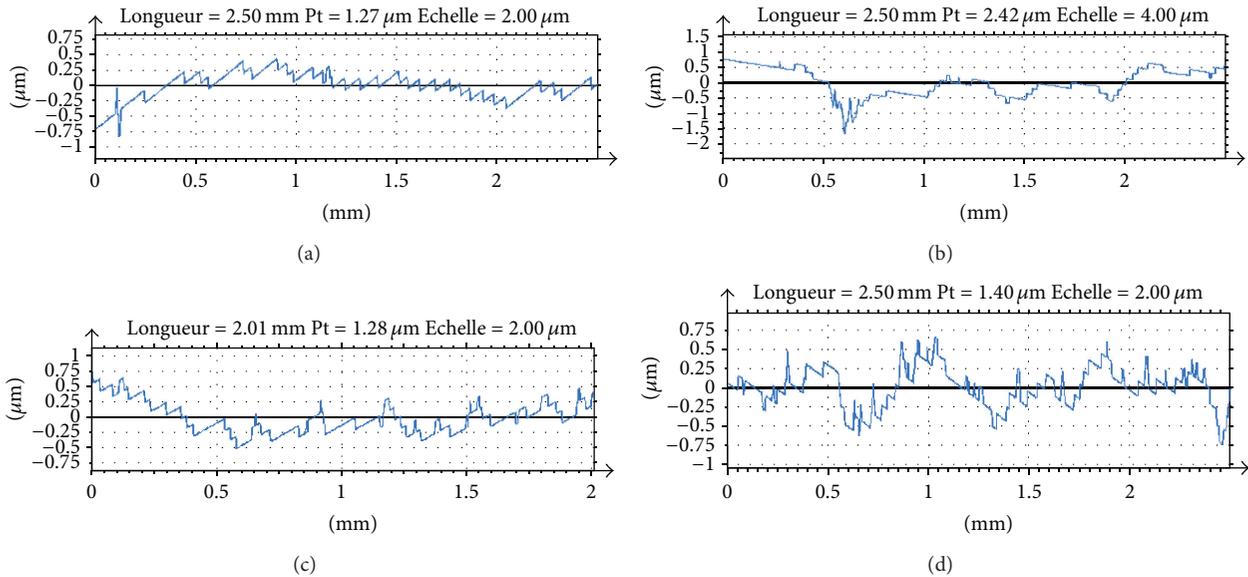


FIGURE 2: Surface profiles of the different primers/topcoat: (a) SP, (b) DP, (c) PP, and (d) AP.

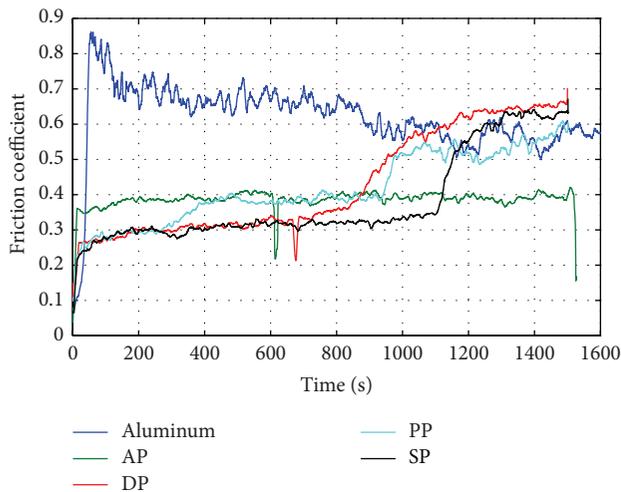


FIGURE 3: Friction coefficient of the studied primers/topcoat applied on the aluminum substrate as a function of sliding time.

of the paint system, which with service time becomes delaminated from the substrate leading to an increase in corrosion.

**3.2.1. Immersion Test in NaCl Solution.** The results obtained for circular scratch specimens after 15 days of exposure in 5% NaCl are shown in Figure 4. The electrogalvanized steel and the nonmetallic coated steel are more susceptible than the two other substrates in terms of delamination without significant penetration of corrosion under the primer coating. The minimum delamination is obtained when the primer is applied on hot-dip galvanized steel and aluminum panels; furthermore, they show no significant signs of corrosion.

Corrosion products were mainly detected after removing the primer from the steel panels. Analysis of Figure 4 suggests that all primers applied on steel, except DP, suffer a significant degradation close to the circular scratch, but at different rates of evolution. Delamination of AP primer is visibly more rapid than the others.

Initially the area that is exposed to the NaCl solution, where the circular scratch was made on the steel panel, suffers corrosion. As the oxide film grows, this scratch behaves as a cathode to neighboring zones in contact with the NaCl solution and function as anodic regions. The  $\text{Fe}^{2+}$  ions in contact with the solution ( $\text{O}_2$  and  $\text{HO}^-$  produced in the cathodic zone) give rise to corrosion products  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}(\text{OH})_3$ , or  $\text{Fe}_2\text{O}_3$  [15, 16] which are retained below the delaminated coating. With the increase in immersion time in the NaCl solution, the anodic zones proceed towards the adjacent zones. This progress is facilitated by the formation of microscopic blisters around the delaminated area. In conclusion, the propagation of corrosion is faster with the steel panel due to the absence of a pretreatment layer (zinc), proposed to enhance metal/paint adhesion [17].

Figure 4 shows that when using steel as substrate, DP/topcoat is the best system. This can be ascribed to the high interface adhesion between them and/or to the high impermeability of the paint system against ions transport [14]. The latter result is confirmed by cupping (Figure 1), impact resistance (Table 4), and lattice method (Table 5).

Zinc is chemically more active than steel; thus the corrosive elements tend to feed upon the zinc, preventing rusting of the underlying steel parts.

In aerated and near neutral pH NaCl solution, the passive layer from zinc does not form [18]. Many studies on the corrosion behavior of zinc in NaCl solutions have been carried out, where the corrosion of zinc proceeds via two partial reactions [18, 19].

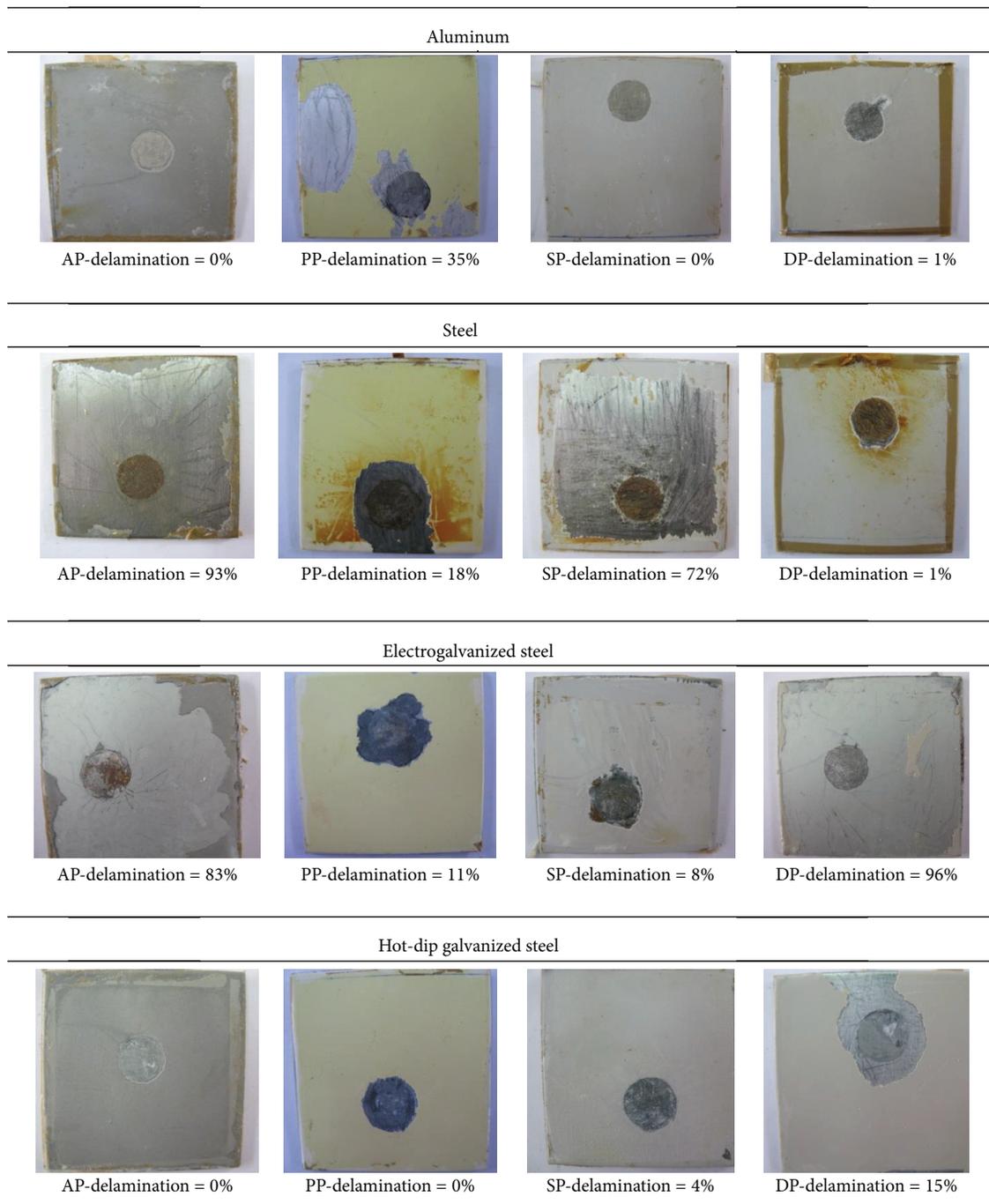
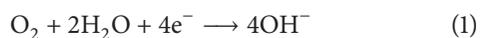
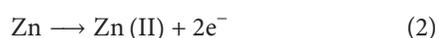


FIGURE 4: Delamination of primers applied on the different substrates after 15 days of exposure in 5% NaCl solution.

- (i) The cathodic reaction corresponds to the reduction of oxygen and leads to a pH increase:



- (ii) The anodic reaction involves the dissolution of zinc and leads to weight loss:



Accordingly, the corrosion layer will occur on the area where the circular scratch was made. This layer is porous and much hydrated, the passivation of zinc does not occur, and the corrosion of zinc will proceed especially under the polymeric coating [18].

Figure 4 shows that, despite the good mechanical properties of different coating systems, delamination is very significant in the case of electrogalvanized steel more so than that of hot-dip galvanized steel. This fact can be related, as

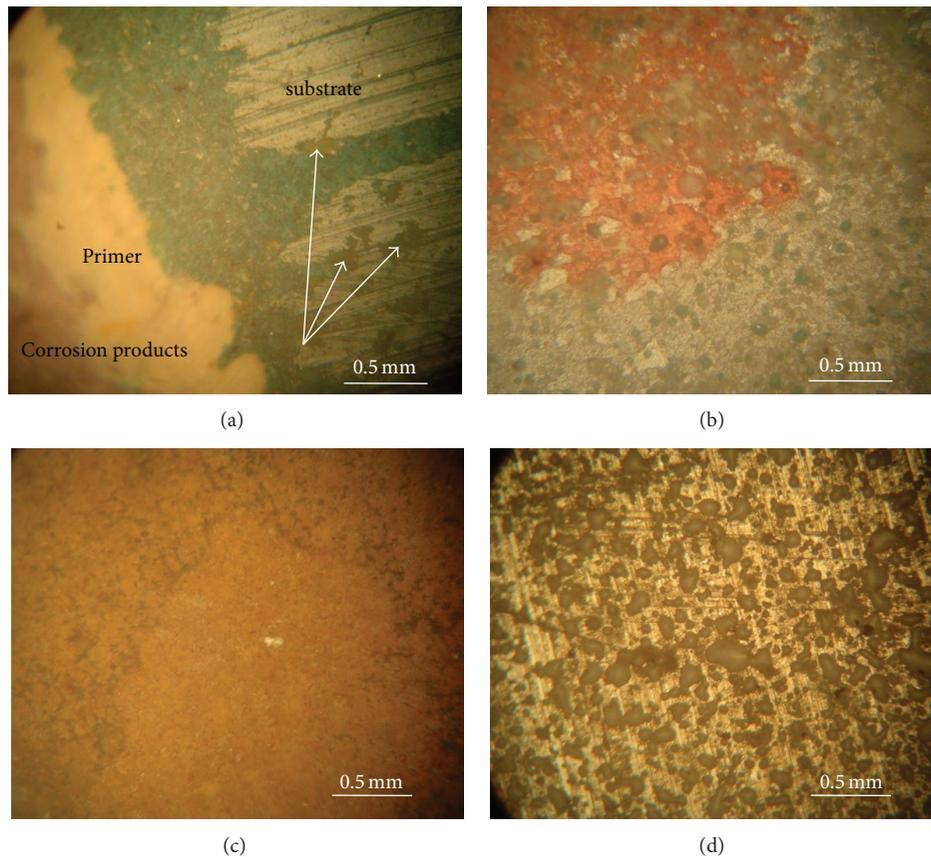


FIGURE 5: Optical micrographs of corroded surface after 15 days of exposure in 5% NaCl solution: (a) primed steel, (b) hot-dip galvanized steel, (c) steel, and (d) aluminium.

mentioned by Delplancke et al. [20], to the poor adherence to the electrogalvanized zinc layer. In the opposite case, the film can only detach locally from the coated substrate.

The corrosion resistance of aluminum arises from its ability to form a natural oxide film on the surface in a wide variety of environments. This oxide film can readily undergo corrosion reactions as has been reported in many investigations into the electrochemical behavior and corrosion resistance of aluminum in different environments and especially the ones containing chloride ion [21].

In NaCl solution (aerated and near neutral pH) we assist the formation of aluminum chlorides,  $\text{AlCl}_3$ , or chloride complexes,  $[\text{AlCl}_4]^-$ , or even soluble oxychloride complexes,  $[\text{Al}(\text{OH})_2\text{Cl}_2]^-$ , which lead to Al corrosion [21].

Polymeric coatings on aluminum are generally subjected to filiform corrosion which usually starts at cut edges [22]. A humid atmosphere is required for filiform propagation, but at relative humidity of greater than 95%, filiform corrosion tends to give way to blistering. There are two main theories for the mechanism of delamination of the coating above the head. One is osmotic disbandment. Several researchers [23–25] accept the possibility that the formation of salts and existence of ions in the filiform head can cause osmotic transfer of water across the film. Slabaugh and Grotheer [24] and van der Berg et al. [25]

claim that this osmotic pressure inside the head is sufficient to cause delamination of the polymer above the metal. There has been recent evidence that the mechanical force from hydrated corrosion products may play an important role in causing delamination and filiform corrosion to advance [26].

Visual inspection of immersed AP, SP, and DP coatings showed no blistering, gloss change, or delamination from the aluminum substrate after 15 days of exposure in 5% NaCl solution (Figure 4). With regard to the mechanical properties no direct conclusions can be retained. Therefore, further study is required to provide a better understanding of which physical and/or chemical interactions are responsible for the adhesion enhancement and the mechanisms for environmental degradation of the interface bonding.

In order to more investigate the corrosion behavior of all the retained substrates and at the interface coating/substrate in NaCl solution, morphology of the corroded surfaces was examined using optical microscopy (Figure 5).

From these optical observations different behaviors can be seen: (i) the delamination interface of primed steel and the initiation of corrosion products at the proximity (Figure 5(a)); (ii) the local dissolution of zinc layer and the corrosion of steel beneath this protective layer (Figure 5(b)); (iii) the generalized corrosion process on steel substrate

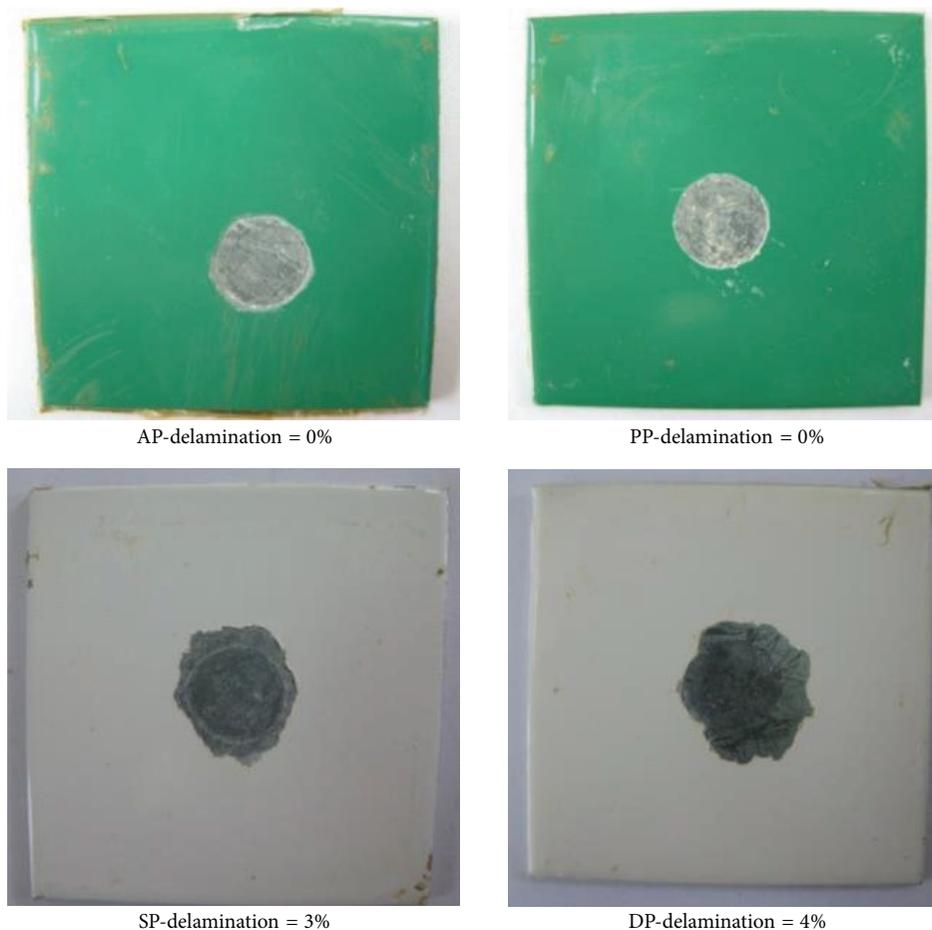


FIGURE 6: Delamination of primer/topcoat system applied on hot-dip galvanized steel after 15 days of exposure in 5% NaCl solution.

(Figure 5(c)); and (iv) the formation of uniform distributed pits on the surface of aluminum substrate.

After topcoat application, coating systems do not exhibit a significant enhancement in anticorrosive behavior after exposure in 5% NaCl solution during 15 days. Primer/topcoat system seems to be subjected to delamination after any defect has occurred. For illustration, Figure 6 shows the delamination of topcoated primed hot-dip galvanized steel.

**3.2.2. Electrochemical Tests in NaCl Solution.** In this section, the coated hot-dip galvanized steel was retained to run electrochemical tests.

The free potential evolution of the steel, hot-dip galvanized steel, and all the retained primers applied on the latter in 5% NaCl solution is presented in Figure 7(a). All OCP curves display the same tendency. The potential decreased at the beginning of the test. The OCP of steel and hot-dip galvanized steel were stabilized at  $-0.68$  mV/SCE and  $-0.98$  mV/SCE, respectively. Turning to the primed hot-dip galvanized steel, it can be seen that the free potential has shifted to more positive values, which suggests the protective action of these layers. The PP and SP primers seem to ensure more corrosion protection from the others.

Figure 7(b) depicts potentiodynamic polarization curves of steel and hot-dip galvanized steel panels covered with the different primers and immersed in aerated 5% NaCl solution. As seen in Figure 7(b) the corrosion potential ( $E_{\text{corr}}$ ) values of all the coated hot-dip galvanized steel panels have shifted to more positive values.

On the other hand, SP and PP primers presented lower  $I_{\text{corr}}$  values. These primers seem to be more protective for hot-dip galvanized steel. Lower  $I_{\text{corr}}$  values for SP and PP primers seem to be related to their organic chemical composition. These measurements need to be complemented by EIS tests to study their behavior for longer periods of time.

**3.2.3. Immersion Test in NaOH Solution.** Literature includes many reports on the way that polymeric materials are easily hydrolyzed in the presence of alkalinity [27]. The objective of this section is to investigate the different coatings' resistance in 3% NaOH solution.

After 7 days of immersion in 3% NaOH solution, all primers were delaminated from their substrates. Figure 5 shows the delamination of primers applied on hot-dip galvanized steel after only 2 days of immersion.

The use of topcoat on different primers improves notably the anticorrosive behavior of the coatings. In fact, Figure 8

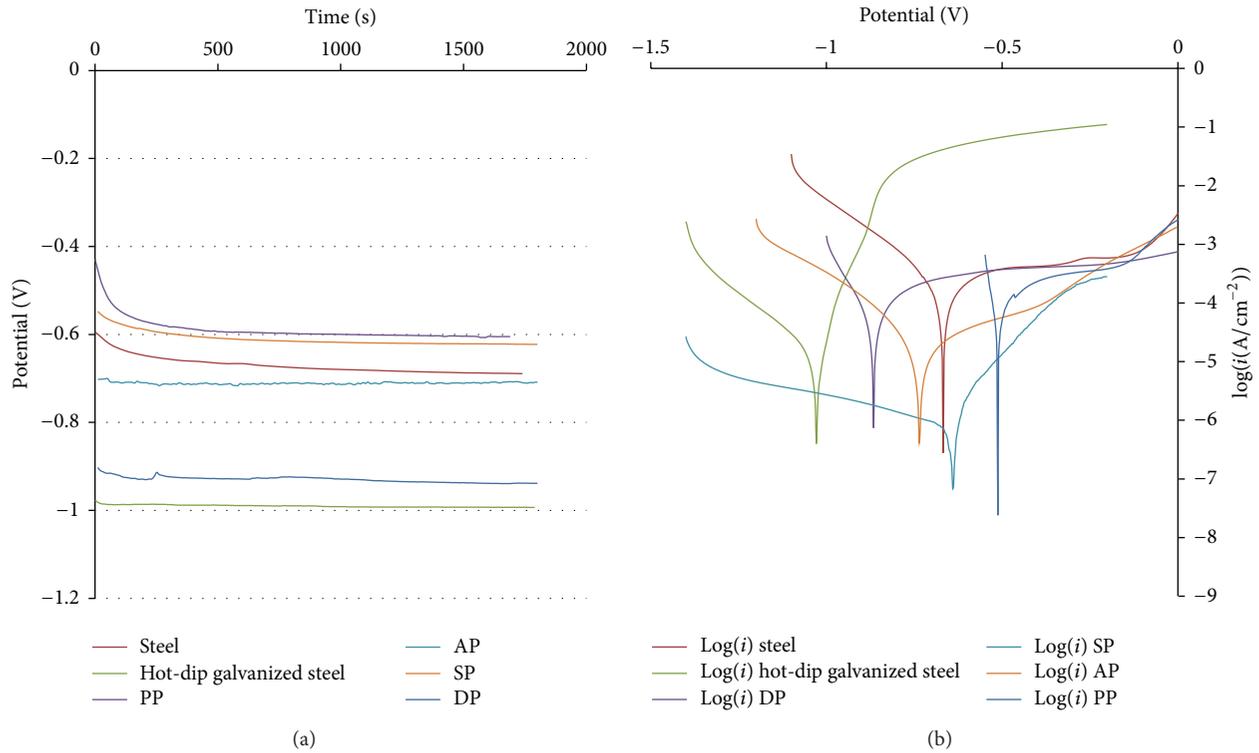


FIGURE 7: (a) OCP evolution of bare steel, hot-dip galvanized steel, and different primers applied on hot-dip galvanized steel immersed in a 5 wt% NaCl solution; (b) potentiodynamic polarization curves of bare steel, hot-dip galvanized steel, and different primers applied on hot-dip galvanized steel immersed in a 5 wt% NaCl solution.

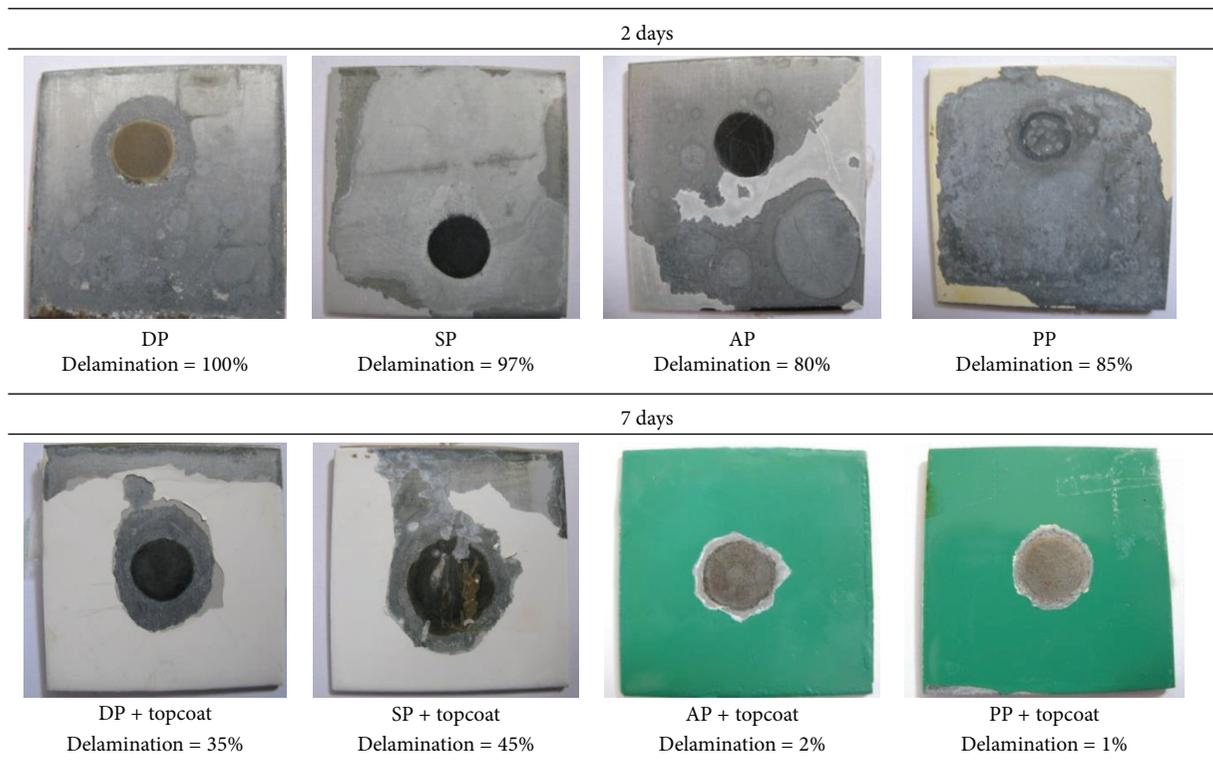


FIGURE 8: Delamination of primers and primer/topcoat systems applied on hot-dip galvanized steel after exposure in 3% NaOH solution.

shows the alkaline resistance enhancement of different systems especially for AP and PP primers.

#### 4. Conclusion

Four commercial automotive primers and a topcoat were applied on different metallic substrates, namely, aluminium, steel, and electrogalvanized and hot-dip galvanized steel. The mechanical, tribological, and anticorrosive performances of the studied coating systems were evaluated. The mechanical characterization shows that (i) all coating systems have a good Persoz hardness, (ii) coating delamination occurs with only aluminum substrate with impact resistance testing, (iii) among the primers, DP has worse cupping behavior, (iv) PP and SP have better flexibility than other coatings, (v) and all coating systems have good adhesion strength.

For tribological test, results revealed, globally, good wear resistance for the whole coating systems.

Immersion tests in 5% NaCl solution show that (i) DP/topcoat is the best system for steel; (ii) hot-dip galvanization is more adequate than electrogalvanization as a pretreatment for steel; (iii) and PP primer is to be avoided on aluminum substrate.

Electrochemical tests in 5% NaCl solution show that PP and SP primers applied on hot-dip galvanized steel present more protective action than DP and AP primers.

Immersion tests in 3% NaOH showed the benefic effect of topcoating in alkaline resistance of different coating systems.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

#### Acknowledgments

This work was supported by “Les Industries de Carrossage Automobiles (ICAR-Tunisia)” and Ministry of High Education and Scientific Research, Tunisia. The authors thank Mlle. E. BEN HROUZ and Mlle M. ESSID, engineers, for help and contribution to this research.

#### References

- [1] N. K. Akafuah, “Automotive paint spray characterization and visualization,” in *Automotive Painting Technology*, K. Toda, A. Salazar, and K. Saito, Eds., pp. 121–165, Springer, Dordrecht, The Netherlands, 2013.
- [2] G. Fettes, Ed., *Automotive Paints and Coatings*, Wiley-VCH, Weinheim, Germany, 1995.
- [3] H. J. Streitberger and K. F. Dossel, *Automotive Paints and Coatings*, Wiley-VCH, Weinheim, Germany, 2008.
- [4] J. V. Koleske, *Paint and Coating Testing Manual: Fourteenth Edition of the Gardner-Sward Handbook*, 1995.
- [5] A. V. R. Kumar and R. K. Nigam, “Mössbauer spectroscopic study of corrosion products beneath primer coating containing anticorrosive pigments,” *Journal of Radioanalytical and Nuclear Chemistry*, vol. 227, no. 1-2, pp. 3–7, 1998.
- [6] M. Lonyuk, M. Bosma, C. A. M. Vijverberg, A. Bakker, and M. Janssen, “Relation between chip resistance and mechanical properties of automotive coatings,” *Progress in Organic Coatings*, vol. 61, no. 2–4, pp. 308–315, 2008.
- [7] J. J. Suay, M. T. Rodríguez, R. Izquierdo, A. M. Kudama, and J. J. Saura, “Rapid assessment of automotive epoxy primers by electrochemical techniques,” *Journal of Coatings Technology*, vol. 75, no. 945, pp. 103–111, 2003.
- [8] R. N. Miller, *Materials Protection*, vol. 7, 1968.
- [9] W. W. Kittelberger and A. C. Elm, “Water immersion testing of metal protective paints: role of osmosis in water absorption and blistering,” *Industrial & Engineering Chemistry*, vol. 38, no. 7, pp. 695–699, 1946.
- [10] G. W. Walter, “Key issues in corrosion control,” in *Proceedings of the 21st Australasian Corrosion Association Conference*, Brisbane, Australia, November 1981.
- [11] J.-I. Moon, Y.-H. Lee, H.-J. Kim, S.-M. Noh, and J.-H. Nam, “Synthesis of elastomeric polyester and physical properties of polyester coating for automotive pre-primed system,” *Progress in Organic Coatings*, vol. 75, no. 1-2, pp. 65–71, 2012.
- [12] R. A. Ryntz, M. Everson, and G. Pollano, “Friction induced paint damage as affected by clearcoat chemistry,” *Progress in Organic Coatings*, vol. 31, no. 4, pp. 281–288, 1997.
- [13] L. Lin, G. S. Blackman, and R. R. Matheson, “A new approach to characterize scratch and mar resistance of automotive coatings,” *Progress in Organic Coatings*, vol. 40, no. 1–4, pp. 85–91, 2000.
- [14] T. Skoulikidis and A. Ragoussis, “Diffusion of iron ions through protective coatings on steel,” *Corrosion*, vol. 48, no. 8, pp. 666–670, 1992.
- [15] M. Pourbaix, *Leçons de Corrosion Électrochimique*, Cebelcor, Brussels, Belgium, 1989.
- [16] A. Bautista, “Filiform corrosion in polymer-coated metals,” *Progress in Organic Coatings*, vol. 28, no. 1, pp. 49–58, 1996.
- [17] E. Almeida, I. Alves, C. Brites, and L. Fedrizzi, “Cataphoretic and autophoretic automotive primers: a comparative study,” *Progress in Organic Coatings*, vol. 46, no. 1, pp. 8–20, 2003.
- [18] M. Mouanga and P. Berçot, “Comparison of corrosion behaviour of zinc in NaCl and in NaOH solutions—part II: electrochemical analyses,” *Corrosion Science*, vol. 52, no. 12, pp. 3993–4000, 2010.
- [19] Q. Qu, L. Li, W. Bai, C. Yan, and C.-N. Cao, “Effects of NaCl and NH<sub>4</sub>Cl on the initial atmospheric corrosion of zinc,” *Corrosion Science*, vol. 47, no. 11, pp. 2832–2840, 2005.
- [20] J. L. Delplancke, S. Berger, X. Lefèbvre, D. Maetens, A. Pourbaix, and N. Heymans, “Filiform corrosion: interactions between electrochemistry and mechanical properties of the paints,” *Progress in Organic Coatings*, vol. 43, no. 1–3, pp. 64–74, 2001.
- [21] E.-S. M. Sherif, “Corrosion and corrosion inhibition of aluminum in Arabian Gulf seawater and sodium chloride solutions by 3-amino-5-mercapto-1,2,4-triazole,” *International Journal of Electrochemical Science*, vol. 6, no. 5, pp. 1479–1492, 2011.
- [22] A. T. A. Jenkins and R. D. Armstrong, “The breakdown in the barrier properties of organic coatings due to filiform corrosion,” *Corrosion Science*, vol. 38, no. 7, pp. 1147–1157, 1996.
- [23] H. Leidheiser Jr., “Corrosion of painted metals—a review,” *Corrosion*, vol. 38, no. 7, pp. 374–383, 1982.
- [24] W. H. Slabaugh and M. Grotheer, “Mechanism of filiform corrosion,” *Industrial & Engineering Chemistry*, vol. 46, no. 5, pp. 1014–1016, 1954.

- [25] W. van der Berg, J. A. W. van Laar, and J. Suurmond, "Advance in organic coatings science and technology," in *Proceedings of the 3rd International Conference in Organic Coatings Science and Technology*, G. D. Parfitt and A. V. Patsis, Eds., pp. 170–187, Athens, Greece, July 1977.
- [26] M. van Loo, D. D. Laiderman, and R. R. Bruhn, "Filiform corrosion," *Corrosion*, vol. 9, pp. 277–283, 1953.
- [27] Y. Takeshita, T. Kamisho, S. Sakata et al., "Mixed powder coating film using thermoplastic polyester and its alkaline resistance," *Journal of Coatings Technology and Research*, vol. 10, no. 4, pp. 503–514, 2013.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

