

# Design and manufacturing of protective barriers on Fe 430 B substrates by phenyl methyl polysiloxane coatings: micromechanical response, chemical inertness, and corrosion resistance

M. Barletta, S. Venettacci, M. Puopolo,  
S. Vesco, A. Gisario

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**Abstract** In the present investigation, scratch resistance, chemical inertness, and corrosion resistance of methyl phenyl polysiloxane coatings on Fe 430 B structural steel with or without an organo-silane intermediate layer were analyzed. The role of Al–Mg pigments dispersed in the resin was studied, too. The high molecular weight of the polysiloxane resin ensures good adhesion to the substrate, low porosity, and high mechanical stability. The good ductility and low steric hindrance of the methyl groups coupled with the chemical inertness of the phenyl groups yields coatings with utmost endurance to aggressive chemicals and, above all, that are suitable as corrosion retardants on sensitive steel substrates. Last, the dispersion in the resin of particles, which act as a corrosion inhibitor, as well as the interposition of organo-silane layers between substrate and polysiloxane resin, can improve further the potential of the designed barrier coatings.

**Keywords** Coatings, Grafting, Inorganic polymer, Manufacturing, Properties and characterization

## Introduction

The chemical structure of organic–inorganic hybrid polymers makes them of utmost interest in the manufacturing of coatings with anti-corrosion features. The

Si–O–Si backbone is highly resistant to aging (i.e., water, saline fog, UV irradiation). The Si–O binding energy of 445 kJ/mol is definitely higher than the corresponding C–C binding energy (358 kJ/mol) of the organic resins. In addition, hybrid organic–inorganic resins are intrinsically self-regenerating, which is of high relevance in delaying the onset of corrosion. The Si–O bond is formed through an equilibrium reaction of hydrolysis and condensation. These reactions are reversible in acid environments, in presence of moisture, or under solar irradiation. New Si–O bonds would be generated according to the equilibrium reaction and the architecture of the resin would remain substantially unaffected.<sup>1,2</sup> Hybrid resins can also covalently bind to metal surfaces, forming resistant Si–O–M bonds by hydrolysis and condensation reaction of alkoxy groups on their side chains with the hydroxyl counterparts, which often reside on the metal surface.<sup>3</sup> Improved adhesion between organic–inorganic hybrid resins and metal confers additional protections against corrosion and improved barrier effects.

However, the design of formulations based on polysiloxane resins and suitable to large-scale applications is often troublesome. Madani et al. showed the route to the manufacturing of corrosion-resistant hybrid organic–inorganic coatings.<sup>4</sup> Fine-tuning of material composition, kinetic of hydrolysis and condensation reactions, catalysts selection, and additives like corrosion inhibitors, plasticizers, and functional fillers was found to be determinant to achieve coatings, which featured long-lasting chemical inertness, and adequate mechanical response (i.e., toughness and high thickness). They also showed how a correct balance between organic and inorganic moieties of the resins should be accurately controlled to avoid highly defective and brittle coatings, with poor chemical endurance.

Among hybrid materials, dimethyl polysiloxanes and methyl phenyl polysiloxanes have seldom been studied to manufacture coatings with good chemical

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M. Barletta (✉), S. Vesco  
Dipartimento di Ingegneria dell'Impresa, Università degli Studi di Roma "Tor Vergata", Via del Politecnico, 1 - 00133 Rome, Italy  
e-mail: barletta@ing.uniroma2.it

S. Venettacci, M. Puopolo, A. Gisario  
Dipartimento di Ingegneria Meccanica ed Aerospaziale, "Sapienza" Università degli Studi di Roma, Via Eudossiana, 18 - 00184 Rome, Italy

inertness and anti-corrosion features.<sup>5–7</sup> Methyl groups can confer good flexibility to the Si–O–Si backbone. The limited steric hindrance of the methyl groups favors the ductility of the resin, especially if compared with the cumbersome epoxy derivatives, allowing the deposition of thick layers. Chen et al. showed that methyl groups together with appropriate co-binders like vinyltriethoxysilane (VTEOS) or aminopropyltriethoxysilane (APTEOS) allow the synthesis of polysiloxane oligomers that can form 35- $\mu\text{m}$ -thick coatings without the addition of other organic derivatives or nano-particles inside the resin.<sup>5</sup> The good flexibility of methyl groups on polysiloxane resins is not compromised by the addition of phenyl groups, as shown by Barletta et al.<sup>8</sup> Indeed, phenyl groups feature larger steric hindrance, and if introduced on the Si–O–Si backbone, make the resulting material stiffer, without increasing further the degree of crosslinking. If the addition of the phenyl groups is finely tuned, they can increase the mechanical response of the resin, without decreasing ductility and toughness. At the same time, the introduction of phenyl groups on the Si–O–Si backbone favors chemical inertness, because phenyls are extremely refractory to react in either acid and alkaline environments, even at high temperature, as a result of the increased stability of the molecular orbits of aromatic organic compounds.<sup>9</sup>

Organo-silanes might act as co-binders inside the organic–inorganic hybrid resin or, alternatively, as interlayer. Appropriate selection of organo-silane compounds influences barrier and anti-corrosion features. If used as co-binders, organo-silanes can crosslink with the organic fraction of the resin to achieve a dense molecular structure, high density of covalent bonds and, thus, an improved shielding against aggressive chemicals or corrosion.<sup>10</sup> Additional examples include the modification of silicone epoxy resin by prehydrolysis with APTEOS. The network formed by the reaction of the epoxy with the amino groups features a molecular structure dense enough to contrast the typical shrinkage of the polysiloxane resin during drying after the coating process, even when coatings of over 30  $\mu\text{m}$  are formed.<sup>11</sup> Further, APTEOS can also covalently bind to the substrate through the alkoxy groups and hydroxyl counterparts on the metal by hydrolysis and condensation. This ensures additional mechanical resistance to the coating system and improved barrier properties in saline solutions (0.05 M NaCl).<sup>11</sup> 3-Glycidoxypropylmethyldiethoxysilane (GPTMS) or trimethylsilyl-2,3,5,6-tetrafluorophenyl (TMSPH) does not ensure similar performance because of limited reactivity with the epoxy counterparts. They were susceptible to major damage in saline environments after a short time range (i.e., within 24 h).<sup>11</sup> In contrast, the deposition of organo-silane interlayers on the substrate can retard the onset of corrosion and improve barrier properties. Some examples include the role of VTEOS interlayers to improve barrier properties of an overlying methyl phenyl polysiloxane resin.<sup>8</sup> Similarly, Bajat et al. showed the improved response of organic barrier coatings on aluminum by interposing an intermediate layer

consisting of prehydrolyzed VTEOS, which was covalently bound with the underlying substrate.<sup>12</sup>

organic–inorganic hybrid resins can also be modified by dispersing functional nano-fillers. Castro et al. tried to disperse silicon oxides,<sup>13,14</sup> Hou et al. zirconium oxides,<sup>15</sup> Feng et al. aluminum oxides,<sup>16</sup> and Padhy et al. titanium oxides.<sup>17</sup> The small particles dispersed in the resin are a discontinuity in the material and act as obstacles to the propagation of the residual stresses, which arise inside the resin during crosslinking. After the coating process and during drying, the resin shrinks because of evaporation of volatile constituents and of molecular rearrangements due to crosslinking. Resin shrinkage causes the onset of stresses inside the material, which can also lead to cracks or, in the worst case, to coating delamination. Nano-particles can oppose additional resistance to the action of residual stresses and avoid premature cracking or failure.<sup>18</sup> In addition, nano-particles can increment the barrier properties as they can interpose in the main chains of the polymeric resin, thus occupying locations which otherwise could represent porosity and, thus, be the source of ion infiltration in aggressive environments.<sup>19</sup> Passivating nano-particles can also act as corrosion inhibitors, thus actively contrasting corrosion.<sup>20</sup>

In the present work, organic–inorganic resins, organo-silane interlayers, and corrosion inhibiting fillers are investigated to manufacture high performance, corrosion retardant coatings. In particular, micromechanical response as well as anti-corrosion and barrier features of a methyl phenyl polysiloxane resin on structural steel substrates are investigated. The role of an organo-silane interlayer and the dispersion of small corrosion inhibiting particles are analyzed. The high molecular weight of the polysiloxane resin, which ensures good adhesion to the substrate, low porosity and high mechanical stability, the good ductility and low steric hindrance of the methyl groups as well as the chemical inertness of the phenyl groups allow the manufacturing of high resistant and corrosion retardant coatings. The dispersion in the resin of particles that act as corrosion inhibitor as well as organo-silane intermediate layers can improve further the potential of the designed barrier coatings.

## Experimental

### Materials

The substrates are flat slabs in structural Fe 430 B steel 40 mm long, 30 mm wide, and 5 mm thick. The hybrid organic–inorganic resin is a modified methyl phenyl polysiloxane (Evonik, Essen, Germany) functionalized with hydroxyl and alkoxy groups on the sides of the main Si–O backbone. Additives like thickeners, flow promoters, wetting agents, and defoamers complete the formulation. The organo-silane is a VTEOS (VTEO, Evonik, Essen, Germany), selected since it

can offer an array of hydrolyzable alkoxy groups plus the crosslinkable organic vinyl group. Metal pigments are commercially available, finely sieved Al–Mg (4.5 wt%) powders (Eckart, Uden, The Netherlands), ~10 µm average diameter of the granulometric distribution, ~0.90 shape factor. Table 1 summarizes the investigated formulations.

### Manufacturing process

Metal substrates were pretreated by a lapping machine with sandpaper (Al<sub>2</sub>O<sub>3</sub>, 400 mesh size) to achieve a smooth and homogenous morphology. Pretreated substrates were washed in an ultrasonic bath of isopropyl alcohol, followed by an additional washing in a solution of an alkaline detergent in demineralized water. The substrates were rinsed with bi-distilled water and dried overnight at 60°C in a convection oven. Pretreated substrates were sprayed (2 bar feeding pressure, nozzle 0.8 mm, stand-off distance 400 mm) with the diluted polysiloxane resin with or without the metal pigments dispersed inside or with a prehydrolyzed solution of VTEOS (2 wt%) in ethanol (96%) and demineralized water. In the former case, the coated substrates were predried for few minutes at environmental conditions (~20°C and 40% HR) and subsequently baked in a convection oven at 250°C for 45 min to crosslink the polysiloxane resin. In the latter case, the organo-silane interlayers were predried for few minutes at environmental conditions (~20°C and 40% HR) and subsequently baked in a convection oven at approximately 100–110°C for 10 min. The organo-silane-coated metal substrates were then recoated with a second layer of

the polysiloxane resin. Predrying for few minutes at environmental conditions (~20°C and 40% HR) was thus followed by baking in a convection oven at 250°C for 45 min. The coatings are summarized in Table 2. Four reference samples in Fe 430 B, uncoated or Zn coated (deposited by hot dipping, cold spraying, electrogalvanizing), with layers of equivalent thickness to the above-mentioned hybrid organic–inorganic coatings, were used for comparative purposes.

### Experimental procedure

Coatings thicknesses and their uniformity were measured by a magnetic inductive gauge (Mega-Check 5FN-ST, List-Magnetik, Leinfelden-Echterdingen, Germany), performing nine measurements equally distributed over the coated surface. The coatings thickness was always designed to fall within the prescribed range of 60–80 µm. In the case of double-layered samples, all the layers were designed to fall within the range of 30–40 µm to get to a final coating thickness included in the prescribed range of 60–80 µm. All the samples that failed to agree with the aforementioned specifications were disregarded.

Cross-cut tape test method according to the ASTM D3359 regulation and pencil test method according to the ASTM D3363 regulations were performed to evaluate coatings adhesion to the substrate and their hardness.

Scratch tests were performed in “progressive load” mode (Micro-Combi, CSM Instruments, Peseaux, Switzerland), using a Rounded Conical Rockwell C diamond indenter, with 800 µm tip radius, 1 mm/min sliding speed, 100 mN–30 N incremental load, and 3

**Table 1: Typical coatings composition**

40 g methyl phenyl polysiloxane resin (Silikophen P80 MPA, Evonik, Essen, Germany)
0.2 g flow promoter (Tego Flow 370, Evonik, Essen, Germany)
0.22 g defoamer (Tego Airex 945, Evonik, Essen, Germany)
0.4 g dispersant (Tego Dispers 685, Evonik, Essen, Germany)
1.8 g corrosion inhibiting pigments (Eckart, Uden, The Netherlands) (only for pigmented layers)

**Table 2: Summary of the designed protective coatings**

Coating codes	Coating steps			
	First step	Second step	Third step	Fourth step
REF	As-received substrate	–	–	–
Type R	As-received substrate	Polysiloxane resin alone	–	–
Type P	As-received substrate	Polysiloxane resin + metal pigments	–	–
Type RP	As-received substrate	Polysiloxane resin alone	Polysiloxane resin + metal pigments	–
V/REF	As-received substrate	intermediate layer of VTEOS	–	–
Type V/R	As-received substrate	Intermediate layer of VTEOS	Polysiloxane resin alone	–
Type V/P	As-received substrate	Intermediate layer of VTEOS	Polysiloxane resin + metal pigments	–
Type V/RP	As-received substrate	intermediate layer of VTEOS	Polysiloxane resin + metal pigments	Polysiloxane resin alone

mm scratch pattern. During the test, the indenter first profiled the surface applying a very low load and recording the starting surface profile (i.e., prescan). Subsequently, the tip penetrated the coating material moving at constant sliding speed and applying the load until the achievement of the scratch pattern (i.e., scan). Normal and tangential forces were recorded accordingly. Finally, the indenter profiled the scratch pattern back at low load to monitor the change in the morphology of the coating after its elastic recovery, storing the residual depth (i.e., post-scan). The residual scratch pattern was rebuilt by the contact inductive gauge of the surface profiler to evaluate the size and geometry of the residual scratch patterns. Scanning electron microscopy (FEG-SEM Leo, Supra 35, Carl Zeiss SMT, Inc., Thornwood, New York) was used to examine the morphology of the residual scratch patterns.

The grade of protection the protective coatings are able to ensure when deposited on Fe 430 B substrates was assessed by accelerated tests with aggressive chemicals. The coated substrates were dipped for up to 1200 h in acid (HCl, 5 wt%), salty (NaCl, 5 wt%), and alkaline (NaOH, 5 wt%) solutions at environmental conditions. The status of the protective coatings was examined for integrity after different testing times.

## Results and discussion

### *Morphology, adhesion and hardness, micromechanical response*

Figure 1 summarizes the SEM images of the coatings. The samples that feature resin without pigments as outermost layer, samples R, V/R, RP, and V/RP, are characterized by a smooth morphology. In contrast, the samples featuring pigments in the outermost layer, samples P and V/P, are characterized by a coarser morphology. Coarseness is determined by the pigments themselves, which, despite being well-distributed in the resin, affect significantly the visual appearance.

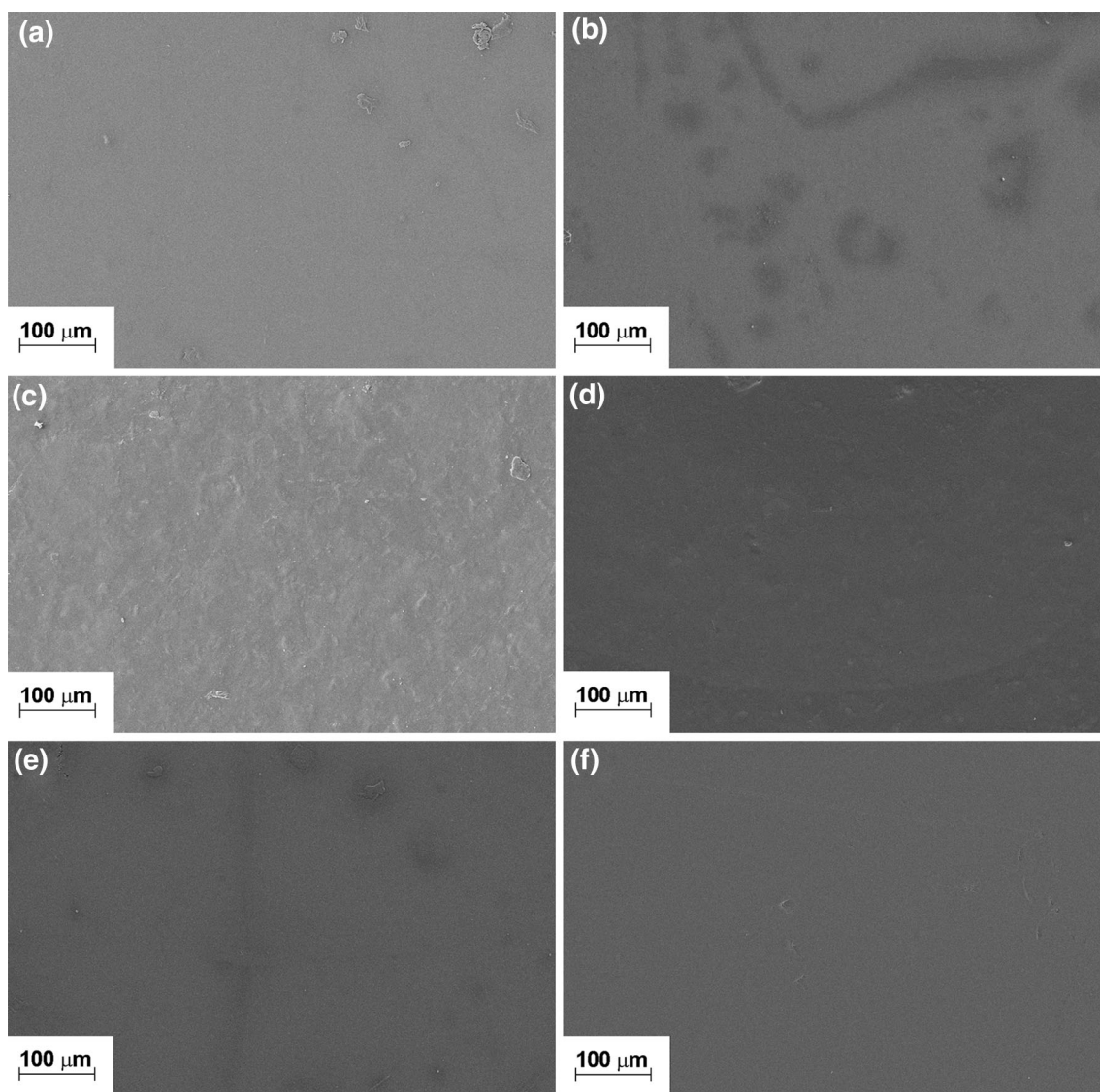
Adhesion tests ensured the good adhesion of all the designed coatings to the substrate, which were classified 5B (that is, 0% of material delaminated after the test). Accordingly, the methyl phenyl polysiloxane resin adhered very well to the underlying metal substrate, regardless of the presence of the organo-silane interlayers. Similarly, the pencil tests showed that surface hardness up to 3–4 H could be achieved.

Figure 2 reports the residual scratch patterns. They have the typical droplet shape, with plastically displaced materials sideways and ahead of the advancing indenter. The coating R which involves the methyl phenyl polysiloxane resin alone is characterized by several fractures. The fractures depart from the very bottom of the residual scratch pattern toward the sides (Fig. 2a). They are C-shaped and directed opposite to the advancing direction of the scratch indenter.

According to Bull,<sup>21</sup> this type of fracture is ascribable to the tensile cracking mechanism. Indeed, when the indenter advances along the scratch direction, it puts under compression the material in front of it, while a concurrent tensile stress acts on the materials at its back. When the tensile stress overcomes the ultimate tensile strength of the coating material, fractures can originate. The fractures are directed opposite the advancing direction of the scratch indenter, as they agree with the distribution of tensile stress in the coating after the contact with the indenter and its recovery in the elastic field.<sup>22</sup> The coating P involves pigments dispersed inside the polysiloxane resin. The pigments can bind with the polysiloxane resin by hydrolysis and condensation of the hydroxyl groups on their surface with the alkoxy and/or hydroxyl counterparts on the side chains of the silicone backbone of the resin. This generates strong covalent bonds, which reinforce the coating against external loads in agreement with references (23,24). In addition, according to reference (25) the good reactivity between filler and matrix prevents the filler from clustering. The coating P, reinforced with the pigments, does not exhibit fractures along the residual scratch pattern (Fig. 2c). The coating RP (methyl phenyl polysiloxane topcoat on an innermost pigmented layer) shows a similar scratch response. No significant fractures are visible on the residual scratch patterns (Fig. 2e). Very small fractures localized around the last contact position between indenter and coating, that is, at very high load, can be seen. However, the fractures are very small and confined to the very bottom of the residual scratch pattern, without propagating toward the sides.

The effect of the organo-silane interlayer can be studied by the residual scratch patterns of the coatings R and V/R (Figs. 2a and 2b). As said, their scratch response is more critical and the coatings were found to fracture under tensile cracking mechanism. The different way to failure of the two coatings allows us to understand the role of the organo-silane grafting polymer. Indeed, the coating R sees the onset of fractures at very low load, that is, at the beginning of the residual scratch pattern. Instead, the coating V/R, which involves the organo-silane interlayer, shows fractures only at higher load, in the middle of the residual pattern, after about 1.5 mm sliding distance. The organo-silane improves the interfacial adhesion of the overlying coatings with the substrate, this playing a role in delaying the onset of fractures during the scratch test. As known, interfacial adhesion between coating and substrate is governed by a multifold mechanism. Mechanical interlocking is ensured by the coarseness of the substrate after lapping. Highly diluted and low viscosity resin after spraying and during the first step of the crosslinking process can infiltrate in the metal asperities, thus generating adhesion by a sort of hook-and-eye mechanism.<sup>26</sup> Coarse structures by lapping at the metal interface can also physically oppose the shearing stress generated inside the coating by the application of external



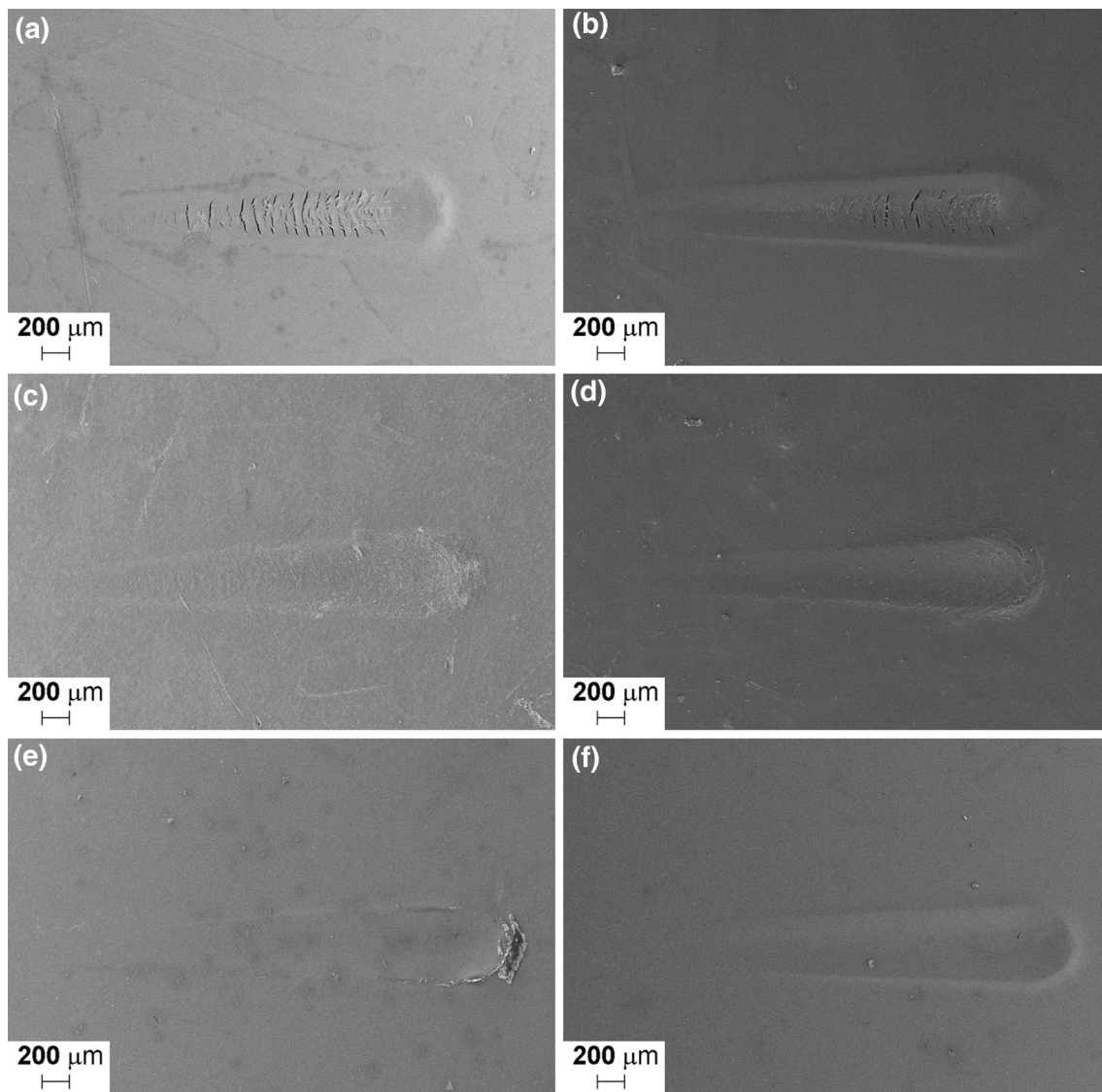


**Fig. 1: SEM images of the coatings surfaces**

loads.<sup>27,28</sup> Lastly, the increase in the contact area between coating and coarse substrate can favor chemical interactions.<sup>29</sup> As shown in reference (3), chemical bonding is ensured by hydrolysis and condensation reaction between hydroxyl functional groups on the metal substrate and hydroxyl/alkoxy counterparts on either the side chains of the methyl phenyl polysiloxane resin or the organo-silane (VTEOS) interlayer. The reaction is favored by the extent of contact between coating and substrate. Nevertheless, while the reactivity of the methyl phenyl polysiloxane on metal can be supposed to be retarded by the relevant steric hindrance of the resin, the smaller VTEOS should easily find its way to the metal surface and combine by forming covalent bonds. According to the same mechanism, VTEOS can also react with the alkoxy/hydroxyl groups of the overlying polysiloxane

resin and form solid covalent bonds with the resin, as well. This should ensure improved adhesion of the coatings on the substrate. In references (30–34), the adhesion between coating and substrate is found to be of utmost relevance to improving the scratch response of a ductile coating on metal. The good adhesion the VTEOS interlayer is supposed to promote between coating and substrate should thus explain the better scratch response of the coating V/R and the delay in the onset of the fractures in the residual scratch pattern.

Figure 3 shows the trends of the residual and penetration depths after progressive load scratch tests. Methyl phenyl polysiloxane coatings showed a good recover capability despite high hardness and adhesion strength to the metal substrate. The coating ductility can be explained in light of the resin architecture. The resin features a stiff siloxane backbone on which



**Fig. 2:** SEM images of the residual scratch patterns, using an 800  $\mu\text{m}$  tip radius indenter for: (a) type R; (b) type V/R; (c) type P; (d) type V/P; (e) type RP; (f) type V/RP

methyl and phenyl side chains are located. The presence of the small steric hindrance methyl groups confers ductility to the coating. In fact, the small methyl groups can still rotate around the siloxane backbone, that is, around the  $-\text{Si}-\text{O}$  bonds and make the resin highly flexible in agreement with reference (35). This is of utmost importance, as the class of protective coatings often see performance compromised by their brittleness, which is pretty common in epoxy, epoxy silicone and, more in general, in organo-silane systems achieved by the sol-gel route.<sup>35–37</sup> In this respect, the presence of the phenyl groups does not disturb significantly the flexible architecture of the resin, and phenyls are potentially useful as they increase the strength of the resin, promote a stiffer response under external loads and, being chemically inert, the overall resin endurance over a long time.<sup>38</sup>

The stiffer response of the pigmented coatings P and RP is confirmed by the lower maximum penetration depth (i.e., approximately 30  $\mu\text{m}$ ). In contrast, the softer coating R exhibits higher maximum penetration depth (i.e., approximately 40  $\mu\text{m}$ ). Residual deformation averages the 50% of the imposed deformation under load, regardless of the coating composition.

The role of the organo-silane interlayer is not easy to discern from the examination of penetration and residual depth trends. However, the general impression is an increase in the stiffness of the coatings involving the interlayer, demonstrated by a slight decrease in the maximum penetration depth (especially in the coatings more susceptible to scratch damage, that is, coatings R and V/R and, less, coatings RP and V/RP). Similarly, the residual scratch patterns of the coatings V/R and V/RP feature slightly decreased residual depths if

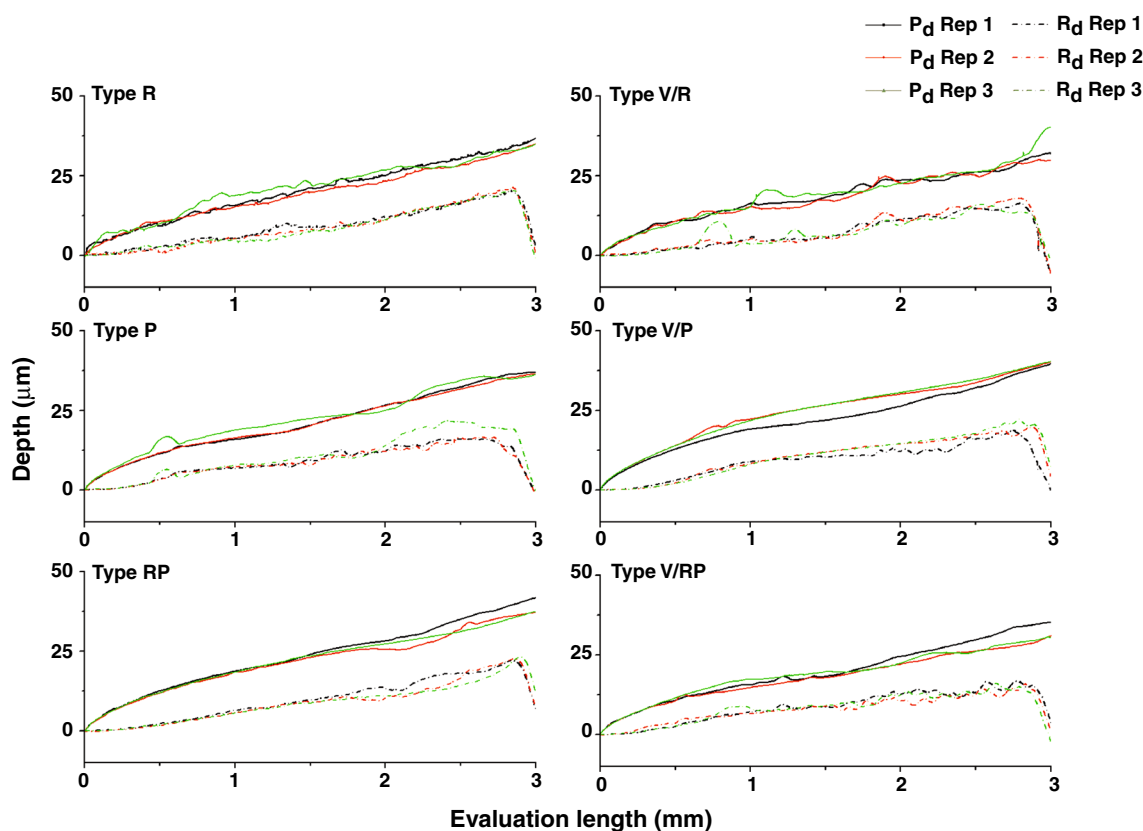


Fig. 3: Trends of the penetration and residual depths for a progressive load scratch test using an 800  $\mu\text{m}$  tip radius indenter

compared with the corresponding coatings R and RP, respectively.

#### ***Endurance to aggressive chemicals: role of coating structure and involved mechanisms***

Table 3 summarizes the response of the protective coatings R, V/R, P, V/P, RP, and V/RP to being dipped in aggressive solutions compared with the as-received and Zn-coated (deposited by hot dipping, cold spraying, electrogalvanizing) Fe 430 B substrates. Salty, acid, and alkaline environments were investigated. While 154 h exposure time is enough to cause failure of the as-received or Zn-coated substrates whatever the investigated conditions, the coatings involving the methyl phenyl polysiloxane resins were not affected. Regardless of the specific design of the coatings, the polysiloxane resins were not impaired until at least 250 h exposure. Because of the high concentration of chemicals used in the solutions (5 wt% of NaCl, HCl, and NaOH), the achieved results are of major relevance. In the literature, comparative protective coatings are often evaluated against blunter conditions, involving lower concentrations (usually, set at approximately 3 wt% in either saline or acid environments<sup>11,39</sup>).

The performance of the protective coatings R, V/R, P, V/P, RP, and V/RP might be ascribed to the intrinsic features of the methyl phenyl polysiloxane resins. Methyl and phenyl groups confer hydrophobic properties to the system,<sup>6</sup> slowing motility and preventing infiltrations of chemical species. The resin is inert, flexible, and can be deposited at high thickness, forming covalent bonds with the metal substrate. This delays corrosion damage and limits the infiltration of the aggressive chemicals at the interface metal-coating as covalent bonds can physically hinder the molecules' passage<sup>11</sup> and, also, inhibit their absorbance, largely responsible for the onset of corrosion.<sup>40</sup> Organo-silane interlayers can further improve the response of the resin. As said, the small steric hindrance of VTEOS can make it react more efficiently with both metal and polysiloxane resins and act as bridging (i.e., grafting) molecules, thus ensuring additional protection.

Figure 4 shows the coatings R, V/R, P, V/P, RP, and V/RP. Figure 5 shows the same surface after 1200 h dipping time in salty solution. The coatings are unaffected by the saline solution. In the acid environment (Fig. 6), the onset of damage by corrosion products occurs after 500 h. The first coatings to be impaired (i.e., with pitting) are the types R (Fig. 6a) and V/R (Fig. 6c) and they involve the polysiloxane



**Table 3: Evolution of corrosion damage during the first exposure of 154 h of the protective coatings in the aggressive environments**

	Exposure time (h)					
	2	5	11	26	90	154
<i>NaCl (5 wt%) salty environments</i>						
Type R	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/R	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type P	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/P	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type RP	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/RP	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
As-received Fe 430 B	Onset	Serious	Severe	Severe	Fail	–
Zn-coated Fe 430 B (electrogalvanizing)	Onset	Onset	Onset	Onset	Serious	Fail
Zn-coated Fe 430 B (cold processing)	Onset	Serious	Serious	Severe	Severe	Fail
Zn-coated Fe 430 B (hot dipping)	Onset	Fair	Fair	Serious	Fail	–
<i>HCl (5 wt%) acidic environments</i>						
Type R	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/R	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type P	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/P	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type RP	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/RP	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
As-received Fe 430 B	Onset	Serious	Serious	Severe	Fail	–
Zn-coated Fe 430 B (electrogalvanizing)	Onset	Serious	Serious	Severe	Fail	–
Zn-coated Fe 430 B (cold processing)	Onset	Fail	–	–	–	–
Zn-coated Fe 430 B (hot dipping)	Onset	Serious	Serious	Severe	Fail	–
<i>NaOH (5 wt%) alkaline environments</i>						
Type R	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/R	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type P	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/P	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type RP	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
Type V/RP	Untouched	Untouched	Untouched	Untouched	Untouched	Untouched
As-received Fe 430 B	Onset	Serious	Fail	–	–	–
Zn-coated Fe 430 B (electrogalvanizing)	Onset	Onset	Fail	–	–	–
Zn-coated Fe 430 B (cold processing)	Onset	Onset	Fail	–	–	–
Zn-coated Fe 430 B (hot dipping)	Onset	Onset	Fail	–	–	–

Response of the investigated coating system against salty, acidic, and alkaline environments

*Onset* activation of the corrosion damage, *fair* first propagation of the corrosion damage, *serious* extended propagation of the corrosion damage, *severe* the corrosion damage covers more than the half of the exposed surface, *fail* rupture of the coatings or uncontrolled spreading of the corrosion damage

resin alone without the metal pigments. The corrosion spreads faster on the coating involving the resin alone (R). The intermediate organo-silane layer (V/R) slows down the corrosion kinetic. In fact, after 650 h dipping time in acid environment, the coating R is affected by larger pitting and, after 800 h the difference between the coatings R and V/R is macroscopic, with the former coating showing greater damage. The coating R is almost completely delaminated, while pitting on the coating V/R is substantially unchanged. After 1200 h dipping time (Fig. 7), the coating R is destroyed and corrosion impairs the underlying metal. Damage on coating V/R is spread and some localized failure can be noted (i.e., dark spot on the coating surface in Fig. 7). The coatings which involve two layers or metal

pigments are substantially unaffected by the acid environment after 1200 h (Fig. 7). Mg–Al metal pigments act as corrosion inhibitors and they can also interpose in the intrinsic porosity of the polysiloxane resin, reducing the permeability to water-driven corrosion species and, thus, delaying the spreading of corrosion products.

The alkaline environment was found to be the most aggressive. However, the coatings showed the onset of damage after approximately 250 h dipping time (Fig. 8). The coating V/R shows some brighter area on the surface after 250 h. They are evidence of the infiltration of the aggressive hydroxyl ions OH<sup>-</sup>. The infiltration can be the result of the contact between the alkaline environment and coating surface, which



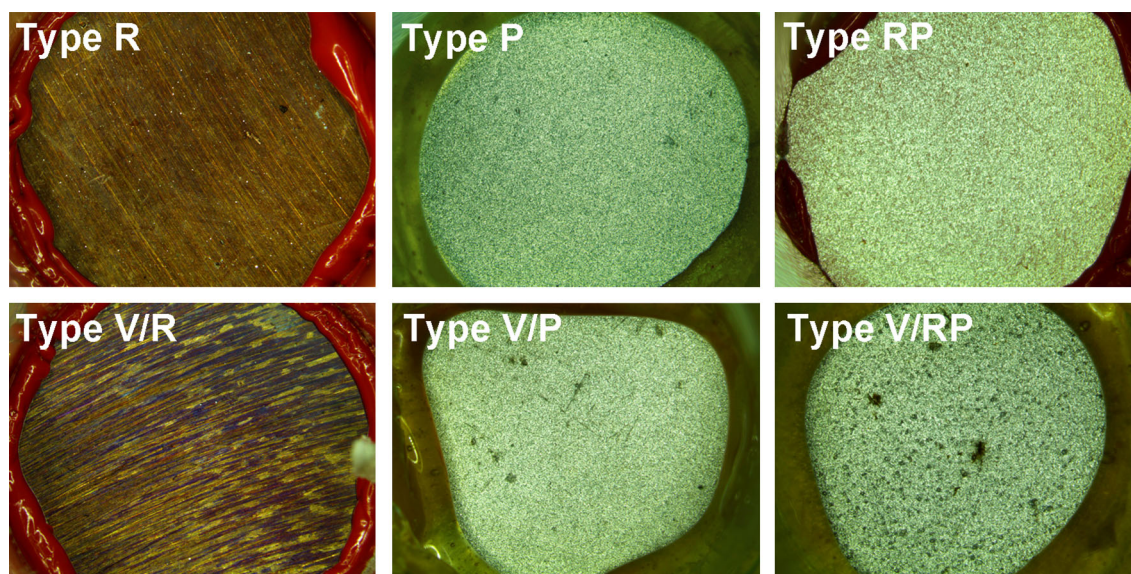


Fig. 4: Surfaces of the protective coatings before dipping in the aggressive chemicals

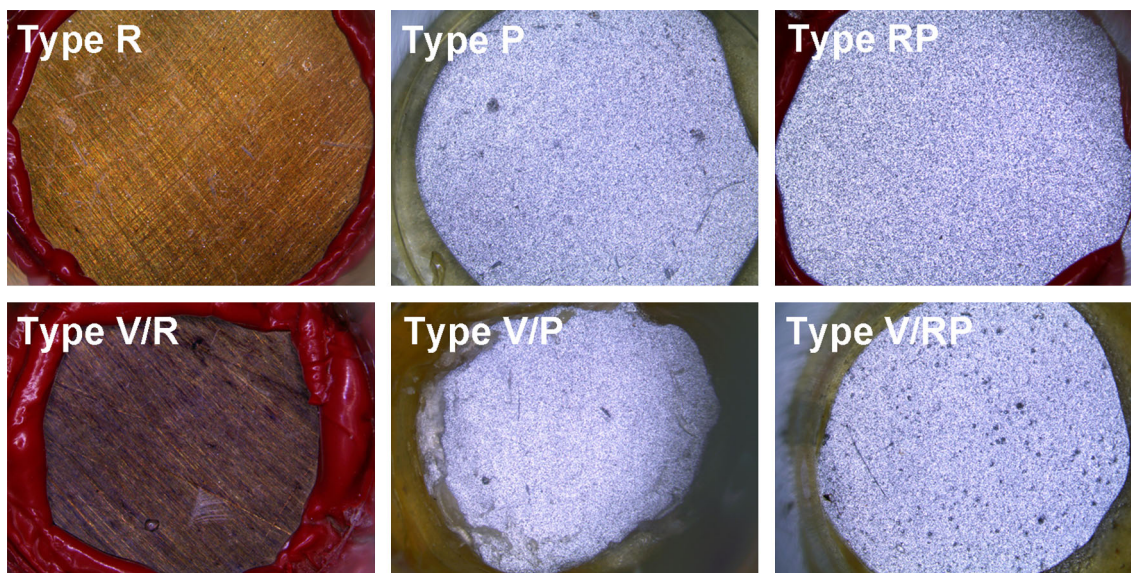


Fig. 5: Surfaces of the protective coatings after being dipped in salty solution (NaCl 5% wt) for 1200 h

compromises the coating flexibility, thus generating very small fractures through which the aggressive species might infiltrate. The coatings, which involve pigments P and, especially, V/P, feature a significant change in color. This color change might be ascribed to the alkaline solution, which impairs the metallic pigments, determining their substantial passivation. This might cause the diffusion of the hydroxyl ions through the new ways generated into the coating at the interface between pigments and polysiloxane resin, thus concurring with the coating damage and embrittlement. The way damage occurs for the double-layered coatings, RP and V/RP, is still different. Pitting

is formed on the coating RP. The aggressive species are able to infiltrate at the interface between the outermost (only polysiloxane) and innermost (polysiloxane + pigments) layer, thus causing the onset of corrosion and generating visible pitting at the interface between the first and second layer. The aggressive species do not seem to infiltrate through the innermost layer, which remains substantially unaffected after approximately 250 h. As regards the coating V/RP, the chemical species can infiltrate at the interface between the two layers (i.e., the outermost polysiloxane and innermost polysiloxane + pigments) and subsequently spread. Infiltrations also take place at the interface between



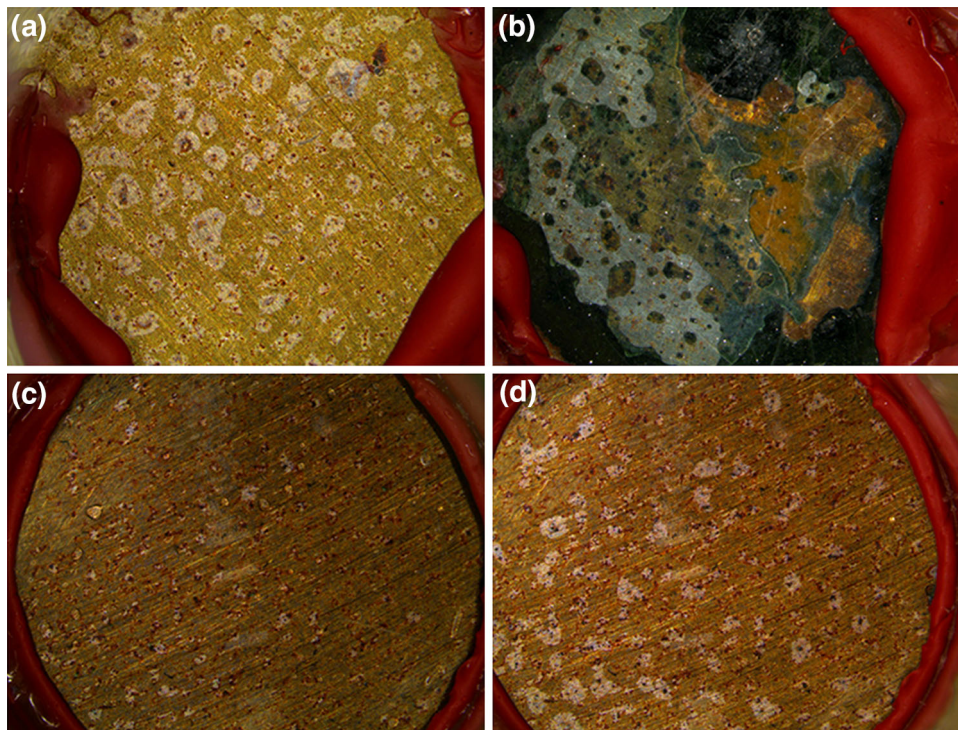


Fig. 6: Surfaces of the protective coatings R and V/R after being dipped in acid solution (HCl 5% wt): (a) type R after 650 h; (b) type R after 800 h; (c) type V/R after 650 h; (d) type V/R after 800 h

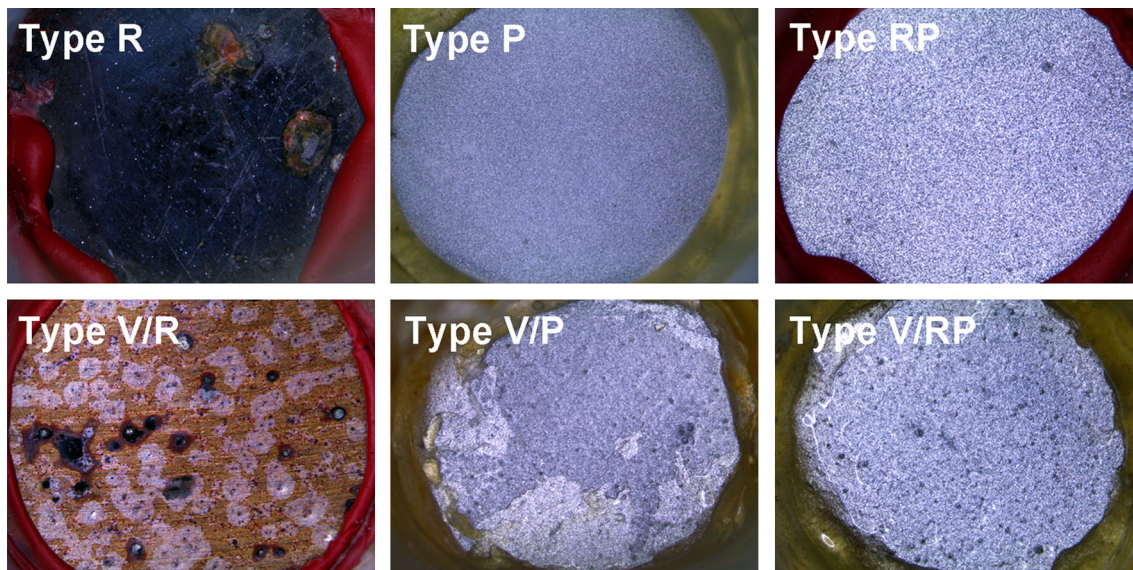


Fig. 7: Surfaces of the protective coatings after being dipped in acid solution (HCl 5% wt) for 1200 h

the innermost resin layer and VTEOS. Thus, the hydroxyl ions can infiltrate down to the metal surface, causing significant damage over large zones of the substrate. Accordingly, the role of the VTEOS inter-layer in the alkaline environment seems to be negative, thus favoring the spreading of corrosion. After 1200 h dipping time in alkaline solutions, the coatings were all

found to be impaired or even collapsed. Indeed, the polysiloxane resin alone (coating R) still shows limited damage, with some brittle fractures spreading on part of the coating surface and some infiltrations at the interface with the underlying metal (Fig. 9a). In contrast, the coating R/V featuring the VTEOS inter-layer exhibits a worse behavior, with wider fractures



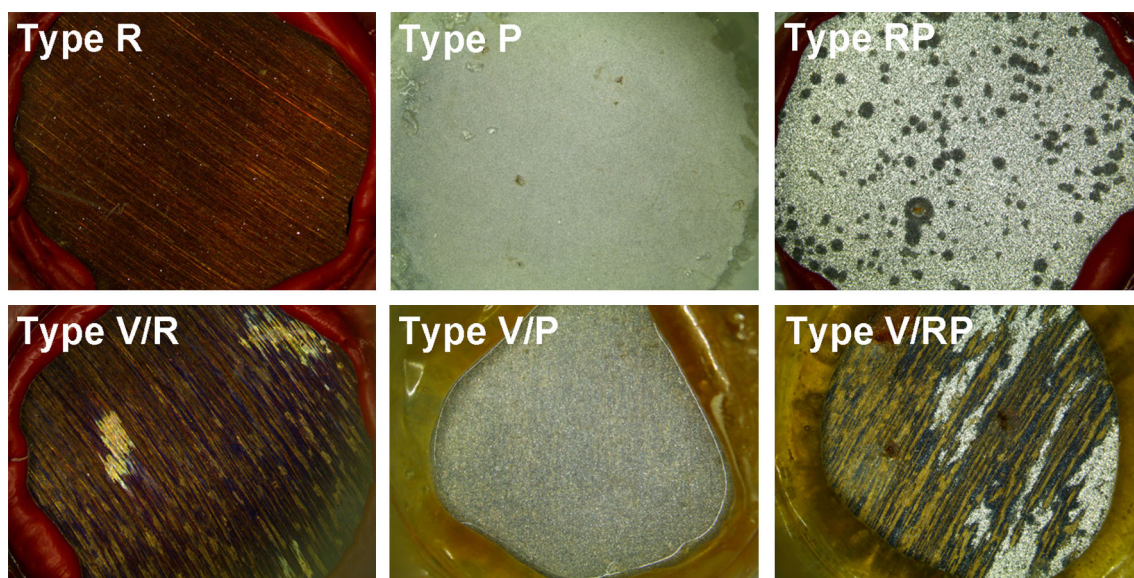


Fig. 8: Surfaces of the protective coatings after dipping in alkaline solution (NaOH 5% wt) for 250 h

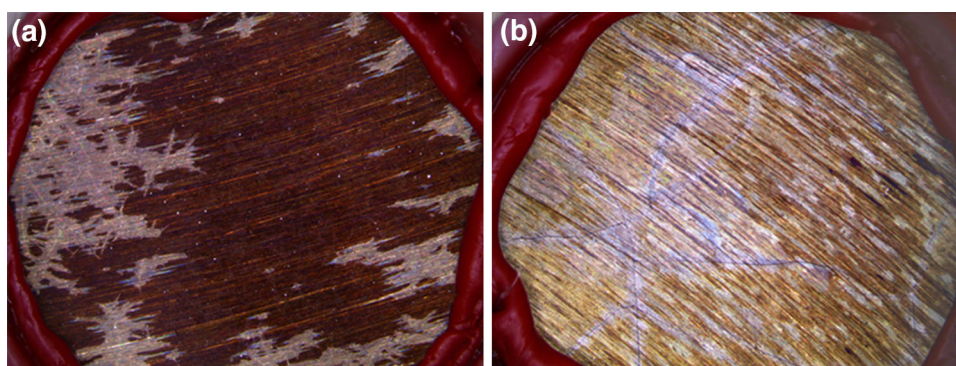


Fig. 9: Surfaces of some protective coatings after dipping in alkaline solution (NaOH 5% wt) for 1200 h: (a) type R; (b) type V/R

spreading over the whole coating surface and infiltrations of the chemical species over the whole interface with the underlying metal (Fig. 9b). This confirms the substantial negative role of the VTEOS interlayer in alkaline environments.

The role of the VTEOS interlayer is thus very influential in establishing the corrosion endurance of the coatings V/R, V/P, and V/RP. In particular, there is a remarkable change in the interlayer effectiveness when chemical endurance is tested in acid or in alkaline environments. As seen in Figs. 6 and 7, the presence of VTEOS interlayers retards corrosion on the metal substrates. In alkaline environments, conversely, the VTEOS interlayers are found to accelerate corrosion (Figs. 8 and 9), induce brittleness of the coatings, and increase absorbance of the water-driven aggressive species at the interface.

Two different mechanisms can be advocated to explain the different responses of the coatings, which

may or may not involve the VTEOS interlayers in acid and alkaline environments. The reactions of hydrolysis and condensation between organo-silane molecules and metals are reversible. The equilibrium of these reactions is at the basis of the good durability of organo-silane systems as a protective barrier when deposited on metals. When the covalent bonds among organo-silanes and metals are impaired for any reason, they can reconstitute, thus restoring the protection at its initial status.<sup>2</sup> The reactions between organo-silane compounds and metals with the formation of Si–O–M bonds as well as the constitution of Si–O–Si bonds are ruled by the pH of the system.<sup>41,42</sup> An alkaline pH causes the orientation of the VTEOS molecules during the application of the interlayer on the metal substrate.<sup>41</sup> In addition, when the pH of the VTEOS formulation involved is higher than the isoelectric point of the metal, the metal itself will be charged negatively. According to an acid–base reaction

mechanism, negative charges will also be generated on the oxygen of the hydrolyzed silane. Under this circumstance, the silane molecules will bind to the metal substrate by orienting themselves to the opposite side and forming a highly hydrophilic layer. This layer would be able to attract water-driven chemical species and, therefore, potentially corroding compounds. This causes a significant reduction in the adhesive toughness of the silane layer, too. Accordingly, when the substrates coated with VTEOS and polysiloxane resins (i.e., coatings V/R, V/P, and V/RP) are dipped inside an alkaline environment (NaOH, 5 wt%), the reactions, which should continuously restore the bonds between organo-silane compounds and metals, are prevented or, at least, hindered by a high pH. In fact, the alkaline environment might negatively charge both the substrate and oxygen through which metal and polysiloxane resin should react and bind, thus slowing down or avoiding the continuous formation or restoration of the Si–O–M bonds. However, different from organo-silane compounds, the higher molecular weights of the polysiloxane resins and their larger steric hindrance hinder the dissolution reactions of the Si–O–M bonds in alkaline environments as they discourage the formation of Si–O–M bonds in neutral environments, thus justifying the long duration of this coating (several hundreds of hours) in caustic soda.

Indeed, the dipping of the coated metals in the alkaline environment and, thus, the presence of OH<sup>-</sup> ions, could also promote the corrosion of the metal according to other routes. Alkaline environments promote the condensation of silane compounds rather than hydrolysis. The condensation reactions favor the formation of larger silane-based networks, which are notoriously more brittle. In contrast, acid environments favor opposite reaction mechanisms, thus improving the coating toughness and flexibility. In fact, a brittle barrier coating is more susceptible to being impaired when exposed to harsh conditions. The subsequent formation of small surface cracks can reduce the barrier effect of the protective coating and allow the infiltration of aggressive chemical species, which could promote faster corrosion. This would support the lower chemical endurance of the coatings V/R, V/P, and V/RP, which involve the VTEOS interlayer, if compared with the ones R, P, and RP, deposited on the as-received metal substrate.

## Conclusions

The present investigations deal with the design and manufacturing of protective coatings based on methyl phenyl polysiloxane resin, corrosion inhibiting pigments, and organo-silane interlayer. Visual appearance and chemical endurance in aggressive saline, acid, and alkaline environments were the focus of investigation. Based on the experimental evidence, the following results can be summarized:

- Methyl phenyl polysiloxane resins can form thick and smooth protective coatings which are transparent and well-adhered to the substrate; organo-silane intermediate layers can further improve the adhesion;
- Coatings which involve pigments dispersed inside the methyl phenyl polysiloxane resin are the best-performing in scratch tests; their better performance is ascribed to the stout network formed by the covalent bonds between pigments and resin and this ensures high resistance to scratch indentation;
- Coatings which involve the methyl phenyl polysiloxane resin alone are ductile, but less scratch-resistant. The ductility is ascribed to the resin structure and, especially, to the presence of the organic methyl groups, which features a very small steric hindrance and allows high mobility to the resin structure;
- Methyl phenyl polysiloxane coatings are highly protective for metal substrates in a saline environment as a result of their high molecular weight which limits the porosity, good ductility at high thickness conferred by the small methyl side chains, and outstanding adhesion to the substrate conferred by hydrolyzable alkoxy groups on their siloxane backbone which prevents infiltration of corroding species at the interface;
- In an acid environment, the hydrolyzable alkoxy groups can react with the hydroxyl counterpart on the metal substrate and, at any time the covalent bonds between the two materials can be affected by the aggressive environments, it can be easily restored by the reversibility of the hydrolysis and condensation reaction;
- In an acid environment, the restoring feature of the Si–O–M bonds favors the coating systems which involve the organo-silane interlayer at the interface between the metal substrate and the overlying polysiloxane resin. The lower steric hindrance of the organo-silane favors the restoring of the Si–O–M bonds;
- Metal pigments are also helpful in an acid environment, as they physically limit the infiltration of the chemical species, interposing themselves in the porosity of the macromolecules, and hindering the permeability to water-driven corrosion compounds. In addition, the coatings which involve the metal pigments, which act as corrosion inhibitor, may ensure long-lasting performance;
- In an alkaline environment, the restoring feature of the Si–O–M bonds is prevented by the pH of the solution in which the coated substrate is dipped. In this case, the organo-silane interlayer can be detrimental, as an alkaline environment can cause its brittle failure and favor the infiltration of potential corroding species at the interface with the metal substrate;
- In an alkaline environment, the coating involving the methyl phenyl polysiloxane resin alone is the



better-performing; the high molecular weight of the resin together with its intrinsic chemical inertness ensure long-lasting performance even after dipping of the substrate in unfavorable environments such as highly concentrated caustic soda solutions.

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