

## Functionalized Polysiloxane Coatings on Hot-Rolled and High-Strength Fe 430 B Steel: Analysis of Mechanical Response and Resistance to Chemicals

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**ABSTRACT:** Hybrid organic-inorganic coatings can be extremely beneficial to improve the performance of steel substrates as their outstanding adhesion strength, scratch resistance, and chemical endurance. However, the design and manufacture of the appropriate coating systems on the different metal alloys can be troublesome. Defective coatings can cause the deterioration of their performance, especially the resistance to aggressive chemicals. In this work, the deposition of functionalized methyl phenyl polysiloxane resins on hot rolled and high strength Fe 430 B steel substrates with and without an intermediate layer of a hybrid organic-inorganic grafting polymer (vinyltriethoxysilane) is comparatively evaluated. Visual appearance, scratch and wear resistance of the coatings as well as their attitude to act as chemical proof barriers are investigated. Proper functionalization of methyl phenyl polysiloxane resins with hydroxyl and alkoxy groups can lead to coatings that are well adhered to the underlying substrates, thus exploiting all the performance they were designed for. In this case, the use of an organo-silane interlayer can further increment the final properties of the overall coating systems. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40624.

**KEYWORDS:** coatings; functionalization of polymers; manufacturing; mechanical properties; surfaces and interfaces

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### INTRODUCTION

Hot-rolled, high-strength steels are widely used in several civil and industrial domains as their good compromise between mechanical and physical properties, accessible costs, and large commercial availability. However, these steels are extremely vulnerable to corrosion and combined erosion-corrosion. In the continental United States alone, the cost of corrosion of metal structures averages one trillion dollars, and it keeps on growing ever faster. Therefore, there is an increasing demand toward reliable solutions to delay corrosion of metals through simple, effective protection technique that could be implemented "*in situ*" and at low cost on the existing structures. In addition, the implementation of protective barriers on products made from different steel grades and before their installation on the field requires operational solutions that should meet the ever stringent specifications imposed by the market. Corrosion protection is usually pursued through the applications on metals of passive or active barrier coatings.<sup>1</sup> Passive barriers are intended to

prevent the direct contact between metal surface and aggressive species like oxygen, water, salts. Active barriers are designed to react themselves with the aggressive species, preventing the underlying substrate to undergo damage.<sup>2,3</sup> Zinc is largely used as active barrier on steel substrates. It can corrode in spite of steel and inhibit the spreading of corrosion damage. Zn barriers are not immune to too aggressive chemicals that can easily dissolve them or infiltrate at interface and, subsequently, attack the underlying metal.<sup>4</sup> Organic coatings can be reliable alternatives to Zn coatings.<sup>5</sup> Composite of metal pigments (Zn, Al, etc.) inside organic resins can be of further interest to prevent corrosion.<sup>6</sup> These barriers interpose a physical protection between metal substrate and aggressive chemicals that can cause corrosion. Nevertheless, organic coatings can be weakly adhered at the interface with the metals (i.e., often only glued on them by mechanical locking). In addition, they are often very soft and, thus, susceptible to mechanical damage, featuring a limited mar/scratch and wear resistance. Accordingly, corrosive solutions or electrolytes can often infiltrate at the interface between

**Table I.** Summary of the Manufacturing Process

	Scenario #1	Scenario #2
Substrate	Fe 430 B	Fe 430 B
Pretreatments	Lapping, washing, drying at 60°C	Lapping, Washing, Drying at 60°C
1st Deposition step	Vinyltriethoxysilane by spraying	Polysiloxane by spraying
1st Crosslinking	Predrying + baking at 100°C for 10 min	Predrying + baking at 250°C for 45 min
2nd Deposition step	Polysiloxane by spraying	-
2nd Crosslinking	Predrying + baking at 250°C for 45 min	-

organic coatings and metal substrates, thus causing the spreading of corrosion products and early failure of the barrier.<sup>5,6</sup>

Hybrid organic-inorganic resins can combine the advantages of the organic resins (especially, ductility, toughness, etc.) with the possibility to covalently bind with the metals, thus overcoming the drawbacks of the poor interfacial adhesion.<sup>7</sup> In particular, a wide range of hybrid organic-inorganic polysiloxanes functionalized with hydroxyl and/or alkoxy groups can react by hydrolysis and condensation with their counterparts on metal surface (i.e., the hydroxyl groups derived from Fe(OH)<sub>3</sub> on steels, Al(OH)<sub>3</sub> on aluminum alloys, etc.), covalently bind to them<sup>8–10</sup> and offer good corrosion protection. Alternatively, many hybrid organic-inorganic grafting polymers based on functional silanes can be used as interlayers to promote the adhesion between metal and polysiloxane coatings.<sup>11</sup> Despite the increased cost of interposing an interlayer and the drawbacks related to the multifold coating procedure, the organo-silanes are endowed with an array of alkoxy groups through which they can easily bind to metals and polysiloxanes at the same time, thus potentially ensuring the best adhesion and protection. The use of silane barriers alone is, however, precluded as their typical high brittleness, even when applied at low thickness on metals.<sup>8</sup>

Appropriate design of protective barriers on metals made from organic-inorganic resins could be of utmost interest. The present investigation comparatively investigates the direct deposition of functionalized polysiloxane resins on hot-rolled and high-strength Fe 430 B steel substrates with a coating system that also involves an intermediate layers based on a hybrid organic-inorganic grafting polymer, vinyltriethoxysilane (VTEOS), to improve the bond between metal and polysiloxane resin. Visual appearance, scratch and wear resistance of the coatings as well as their attitude to act as chemical proof barriers are evaluated. Proper functionalization of polysiloxane resins with hydroxyl and alkoxy groups can lead to coatings that are well adhered to the underlying substrates, thus, exploiting all the performance they were designed for. In this case, the use of an interlayer can further increment the final properties of the overall coating systems.

## EXPERIMENTAL

### Materials

The metal substrates are slabs in Fe 430 B steel 40 mm long, 30 mm wide, and 5 mm thick. The hybrid organic-inorganic resin is a modified phenyl-methyl polysiloxane (Evonik, Essen,

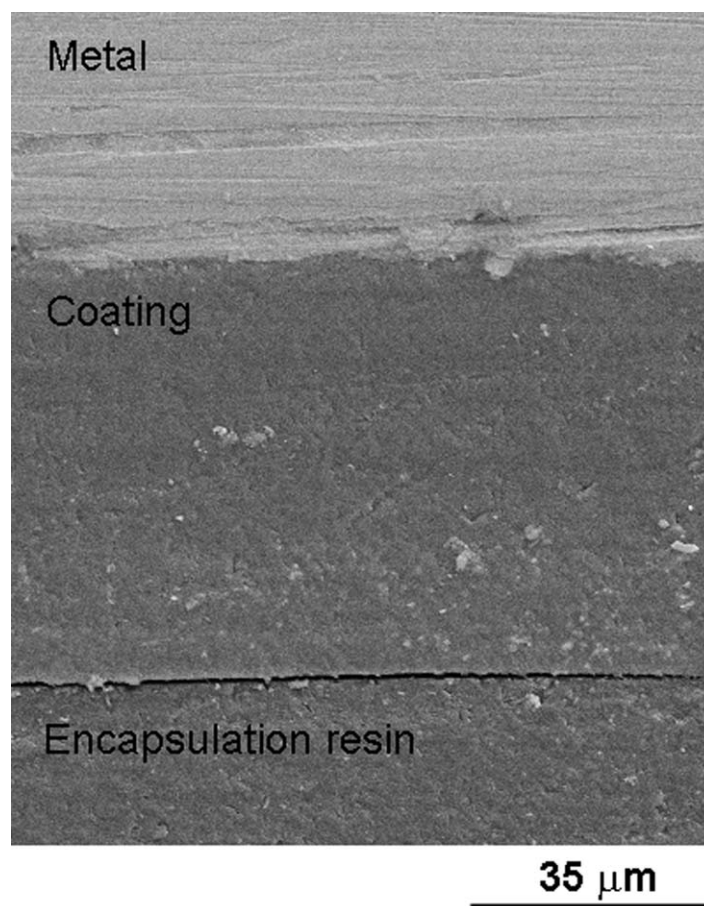
Germany) functionalized with hydroxyl and alkoxy groups on the sides of the main Si—O backbone. The polysiloxane resin is a clear to slightly hazy liquid, with a nonvolatile content of approximately 50%. The viscosity at ambient conditions is approximately 30 mPa s. The organo-silane is a VTEOS (Evonik), selected as it can offer an array of hydrolysable alkoxy groups plus the cross-linkable organic vinyl group.

### Manufacturing Process

Metal substrates were polished by a lapping machine with a solution of fine Al<sub>2</sub>O<sub>3</sub> powder in demineralized water dispersed on a soft cloth until a fairly smooth and homogenous morphology was achieved. Pretreated substrates were then washed in an ultrasonic bath of isopropyl alcohol, followed by an additional washing with a bath of alkaline detergent in demineralized water. The samples were rinsed with bidistilled water and dried at 60°C in convection oven. Pretreated substrates were sprayed (2 bar feeding pressure, nozzle 0.8 mm, stand-off distance 400 mm) with diluted polysiloxane resins 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 baked in convection oven at 250°C for 45 min. In the latter case, the silane coatings were predried for few minutes at environmental conditions (~20°C and 40% HR) and subsequently baked in 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) and baking in convection oven at 250°C for 45 min completed the latter deposition process. Table I summarizes the manufacturing process, and Figure 1 shows the cross-section of a double-layered coating (VTEOS + polysiloxane). Four reference samples in Fe 430 B, uncoated or Zn coated (deposited by hot dipping, cold spraying, electro-galvanizing), with layers of equivalent thickness to the aforementioned hybrid organic-inorganic coatings, was used for comparative purposes.

### Experimental Procedure

Coatings thickness and their uniformity was evaluated by a digital palmer (Mitutoyo, 293–816), performing nine measurements equally distributed over the coated surface. Coatings morphology was analyzed by contact inductive gauge of a CLI profiler (TalySurf CLI 2000, Taylor Hobson, Leicester, UK). In particular, 2000 profiles, 4 mm long, were stored for each sample, with



**Figure 1.** Cross-section of a VTEOS + Polysiloxane coating.

the resolution of  $1\ \mu\text{m}$  along the measurement direction, covering an area  $4 \times 4\ \text{mm}^2$ . Stored profiles were elaborated using the TalyMap 3.1 software, and main roughness parameters were evaluated. A Field Emission Gun-Scanning Electron Microscope (FEG-SEM Leo, Supra 35, Carl Zeiss SMT, Thornwood, New York) was used to examine the visual appearance and coatings morphology.

Scratch tests were performed on the protective coatings, operating in “progressive load” mode (Micro-Combi, CSM Instruments, Peseaux, Switzerland), using a Rounded Conical Rockwell C diamond indenter, with  $800\ \mu\text{m}$  tip radius,  $1\ \text{mm}/\text{min}$  sliding speed,  $100\ \text{mN}$  to  $30\ \text{N}$  incremental load,  $3\ \text{mm}$  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 morphology of the coating after its elastic recovery, storing the residual depth (i.e., postscan). 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. SEM was used to examine the morphology of the residual scratch patterns.

Wear endurance of the coatings was assessed by ball-on-flat linear reciprocating tribological tests (Tribometer, C.S.M. Instruments, Peseaux, Switzerland), using spherical counterpart ( $6\ \text{mm}$  in diameter, 100Cr6 steel). Several tests were performed on each coating by applying  $1\ \text{N}$  normal load,  $3\ \text{Hz}$  frequency,  $6\ \text{mm}$  stroke, and sliding distance up to  $500\ \text{m}$ . The friction coefficients were recorded, as well. The residual worn patterns were rebuilt by the contact inductive gauge of the profiler (resolution  $2\ \mu\text{m}$ ) to evaluate their average depth and the overall volume of the abraded material. SEM was used to examine the residual wear patterns.

The grade of protection of the protective coatings is 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  $154\ \text{h}$  in acid (HCl,  $5\ \text{wt}\%$ ), salty (NaCl,  $5\ \text{wt}\%$ ), and alkaline (NaOH,  $5\ \text{wt}\%$ ) solutions at environmental conditions. The status of the protective coatings was examined for integrity after different testing time ( $2, 5, 11, 26, 90, 154\ \text{h}$ ) and pictures corresponding to the status of the exposed samples surface were stored.

## RESULTS AND DISCUSSION

### Visual Appearance and Morphological Features

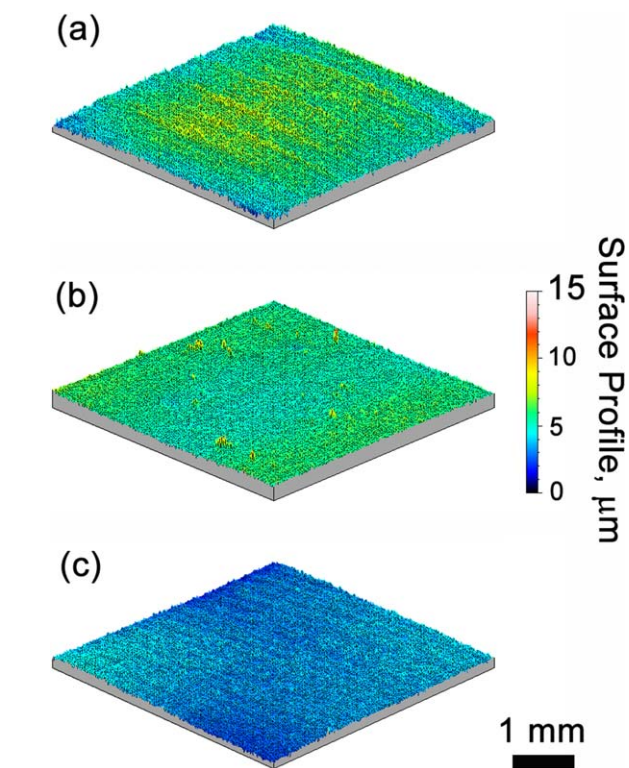
The manufacturing of the coatings was designed to achieve constant and uniform thickness as their mechanical and chemical

**Table II.** Coating Thickness and Average Roughness for the Polysiloxane Coating Alone and VTEOS Interlayer + Polysiloxane Coating System

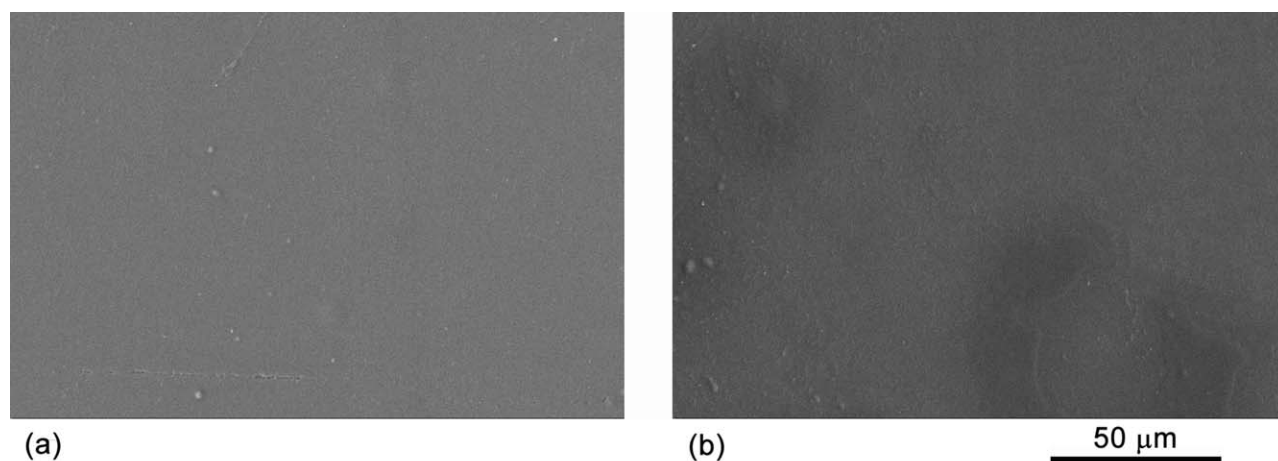
Coatings	Thickness ( $\mu\text{m}$ )	Average roughness $R_a$ ( $\mu\text{m}$ )
Fe 430 B substrate	-	$0.45 \pm 0.01$
Polysiloxane alone	$\sim 62 \pm 4$	$0.16 \pm 0.01$
Vinyltriethoxysilane + polysiloxane	$\sim 69 \pm 7$	$0.18 \pm 0.02$

performance are well known to be strongly dependent on it. According to UNI EN ISO 1461/2009, protective coatings feature a thickness of more than  $50 \mu\text{m}$ . In the present investigation, a useful range of  $60\text{--}70 \mu\text{m}$  was selected for both the functionalized methyl phenyl polysiloxane and VTEOS + functionalized methyl phenyl polysiloxane coatings (Table II). Spraying process was controlled to achieve variations in the coating thickness well within 10%. All the samples which failed to agree with the aforementioned specifications were discarded.

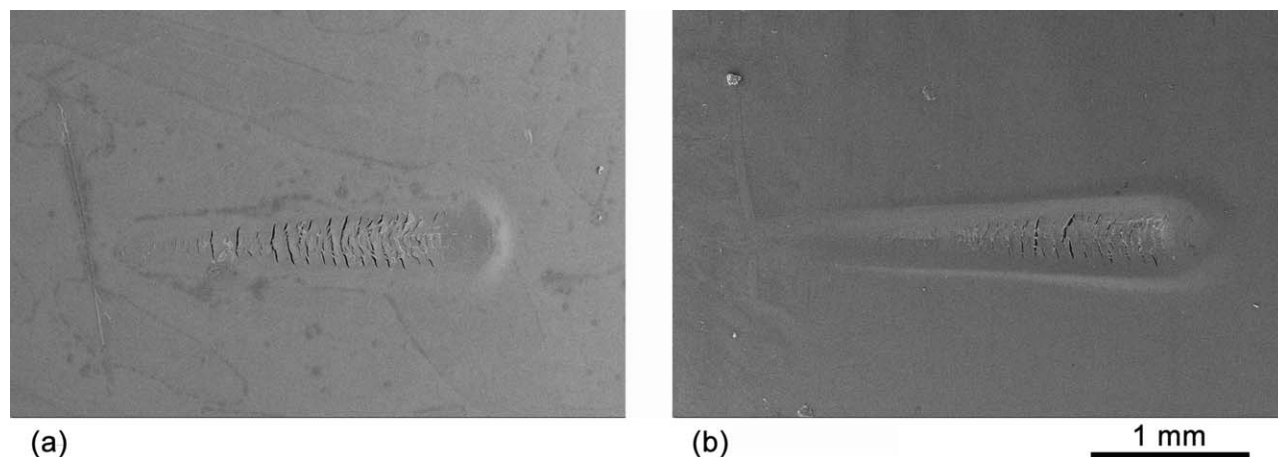
Figure 2 shows the visual appearance of the coatings at high magnification (SEM images). The coatings feature a good finishing without major defects that could affect their mechanical and chemical performance. The coatings are fairly smooth, homogeneous over the surface and not influenced by the interposition at the interface of the VTEOS layer. The application of the coatings on the metal surface modifies significantly the starting morphology. The as-received substrates feature average roughness  $R_a$  of approximately  $0.45 \mu\text{m}$ . After the deposition of the coatings with or without the VTEOS interlayer, the morphology becomes smoother. The average roughness of the two coating systems reduces to less than  $0.2 \mu\text{m}$  (Table II). The smoothing of the starting morphology of the coatings can be attributed to the resin formulations. When the diluted resins are sprayed on the metal surface, they wet intimately the substrate as a result of their features (i.e., chemical affinity with the underlying substrate). In addition, the dilution is designed to

**Figure 3.** Three-dimensional maps of coating morphological features; (a) as-received Fe 430 B substrate; (b) polysiloxane coating alone; and (c) VTEOS interlayer + polysiloxane coating. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

keep fairly low the viscosity of the resin when it enters in contact with the metal substrate, thus allowing the resin to rapidly flow over the surface. In this way, the resins fill all the gaps of the rougher topography of the starting metal surface, thus leading to a general smoothing of the morphological features. Figure 3 shows the three-dimensional maps of the coating morphologies, where the transition from the starting topography of the metals characterized by the parallel stripes due to the

**Figure 2.** SEM images of the coating surface: (a) polysiloxane coating alone and (b) VTEOS interlayer + polysiloxane coating.





**Figure 4.** SEM images of the residual scratch patterns: (a) polysiloxane coating alone and (b) VTEOS interlayer + polysiloxane coating.

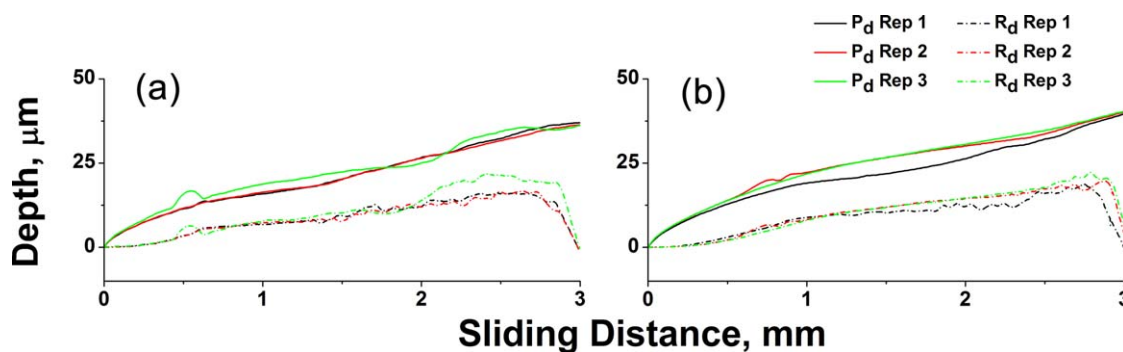
pretreatment with the lapping machine is replaced by the flatter topography of the cross-linked resins.

#### Analysis of the Scratch and Wear Response

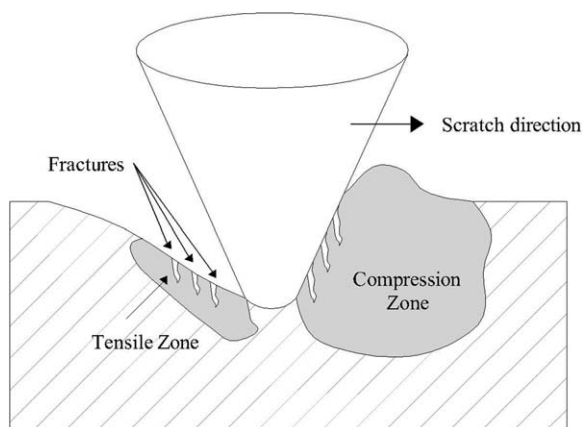
Mechanical response of the coatings was investigated by progressive load scratch and wear tests. The response of the coatings to the scratch indentation was substantially similar whether the VTEOS layers were interposed or not between the functionalized methyl phenyl polysiloxane resins or not. Figure 4 shows the residual scratch patterns. The geometry of the scratch pattern is typical of coating materials that exhibit a substantial elasto-plastic response as also confirmed by the trend of residual and penetration depths reported in Figure 5. The scratch pattern features a drop shape as a result of the incremental load (i.e., maximum penetration and residual depths of 40 and 20  $\mu\text{m}$ , respectively) imposed during the tests, with side and front pile-up of coating materials displaced there by the advancing indenter (i.e., permanent deformation). This deformation mechanism is typical of organic materials deposited on a stiff substrate and featuring a fairly ductile response in agreement with 12. In the present investigation, this ductility should be ascribed to the intrinsic features of the designed coatings. The selected polysiloxane coatings possess organic methyl and phenyl side groups which are designed to confer improved ductility to the overall resin structure. In addition, the polysiloxane resin is

designed to be deposited on metal substrates with large thickness (several tens of micron), thus interposing a thicker barrier between the penetrating indenter tip and metal surface as shown in 13. The resulting coatings are able to deform under the application of the scratch load and, then, recover, even more than 50% of the imposed deformation as confirmed by the examination of the trends of the penetration and residual depths in Figure 5. Differently, many hybrid organic-inorganic coatings feature a different scratch response with a significant brittle contribution, usually ascribed to the intrinsic stiffness and fragility of the polysiloxane backbones, which exhibit a glass-like behavior.<sup>14,15</sup> In addition, hybrid organic-inorganic coatings are usually applied with very low thickness (few microns) as thicker layers would involve too much high internal stresses due to resin shrinkage after cross-linking or self-drying and, potentially, film failure.<sup>16</sup> When stiff substrates are coated, low thickness is not favoring a ductile response of the scratched coatings, as the very thin barrier interposed between the indenter tip and underlying stiff substrate is not helpful enough to relieve the highly concentrated stress imposed during the scratch indentation as shown in Refs. 17,18.

Fracture mechanics is common for the polysiloxane and VTEOS-polysiloxane coatings, as well. The fractures are  $\eta$ -shaped and oriented in the advancing direction of the indenter during

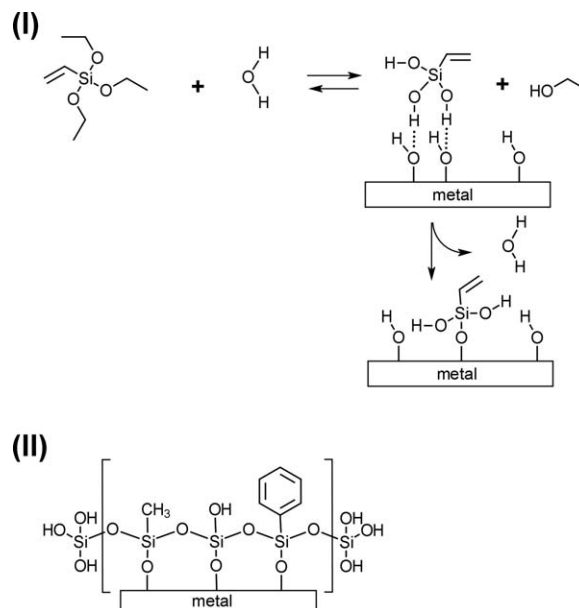


**Figure 5.** Trends of the penetration and residual depths during a progressive load scratch test: (a) polysiloxane coating alone and (b) VTEOS interlayer + polysiloxane coating. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** Stress-field distribution and onset of tensile cracking inside a coating during progressive load scratch test.

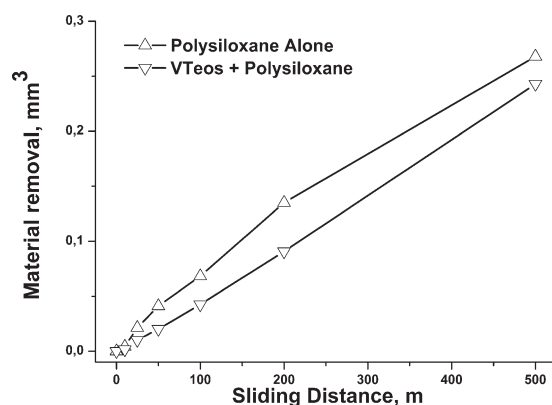
the scratch tests. These geometrical features of the fractures are typical of the tensile cracking fracture mechanism on ductile elasto-plastic materials according to Ref. 19. Tensile cracking originates from the tensile stress that arises at the back of the indenter when it penetrates the coating in its advancing motion (Figure 6). When the tensile stress is sufficiently high to overcome the ultimate tensile strength of the coating, fractures do ultimately occur. In the present cases, fractures are small and located at the very bottom of the residual scratch patterns, where the load concentration is the highest. The size of the cracks is sufficiently small and the penetration and residual depth trends are unaffected, not featuring sudden jumbling in their trends or any other evidence of the cracks onset (Figure 5). However, the onset of the tensile cracking is different for the coatings that involve the VTEOS interlayer or not. In the former case, the onset of the cracking is delayed, and it occurs at approximately half of the scratch pattern (i.e., presumably at ~12–15 N applied load). In contrast, cracking takes place pretty soon on the functionalized polysiloxane resin alone. Being the geometry of the two coating systems approximately the same, the different response can be attributed to the disparity in the chemical bonding established. In the former scenario, the VTEOS interlayer is potentially able to bind by a reaction of hydrolysis and condensation with both the underlying metal substrate through the hydroxyl groups [Fe(OH)<sub>3</sub>] and the overlying polysiloxane resin through the hydroxyl and alkoxy groups featured on the side chains of the Si—O backbone. In addition, the prehydrolyzed VTEOS can form an organic-inorganic network as its ethoxy groups can react internally and, potentially, the vinyl groups, too.<sup>20</sup> This network could act as further relieve barrier to the stress imposed to the overall coating system during the scratch indentation. In contrast, the polysiloxane can react with the underlying metal substrate by a reaction of hydrolysis and condensation through its alkoxy and hydroxyl groups with the corresponding hydroxyl counterparts on the metal surface. Nevertheless, it could be speculated that the reaction process can be partially slowed down by the steric hindrance of the bigger polysiloxane chains compared with the shorter and highly reactive VTEOS molecules or related smaller networks that could combine easily by “*in situ*” grafting



**Figure 7.** Structure of VTEOS and polysiloxane and involved chemism.

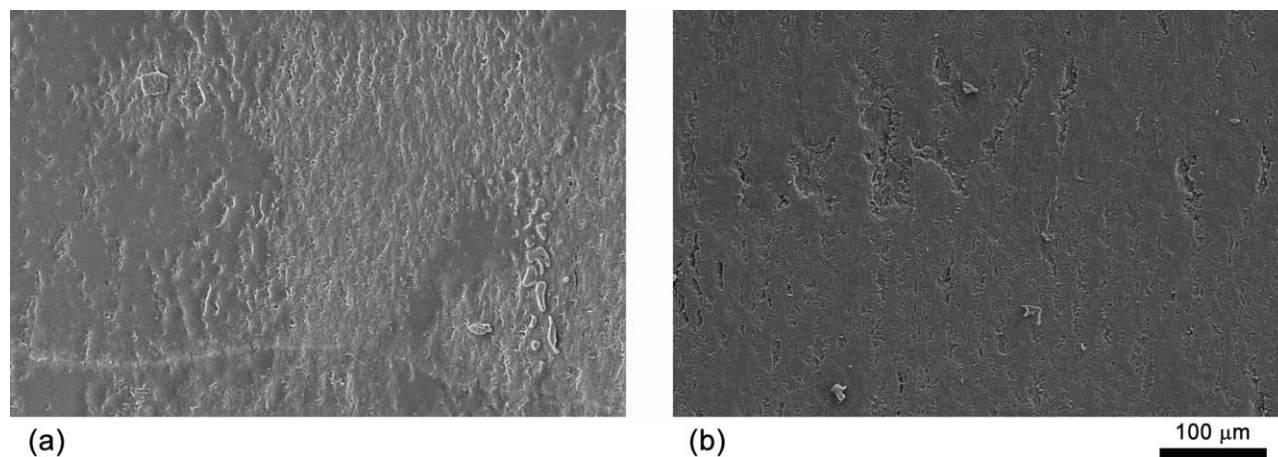
reactions.<sup>21</sup> A sketch of chemical arrangements in the case of the systems involving or not the VTEOS interlayer is reported in Figure 7.

Wear response of the coatings is fairly similar to their scratch response. As a matter of fact, the coatings that involve the usage of VTEOS interlayers are less sensitive to material removal during dry-sliding tribological tests against metal counterpart. The difference with the polysiloxane coatings alone are not huge (Figure 8). However, significant dissimilarities are already perceptible after short sliding distance and confirmed even after the longest sliding distance of 500 m. Once again, the better wear response of the coating system that involves the interlayer can be ascribed to the better chemical bonding between coating and underlying substrate. Although the tribological tests mostly involve the outermost layers of the coating, the response is influenced by the coating structure and, obviously, by the adhesion at the interface with the underlying substrate. Therefore, coatings featuring VTEOS interlayers are better able to withstand the action of the metal counterpart during the tribological tests and, thus, less extent of material is worn out.



**Figure 8.** Trend of material removal during dry-sliding tribological tests.



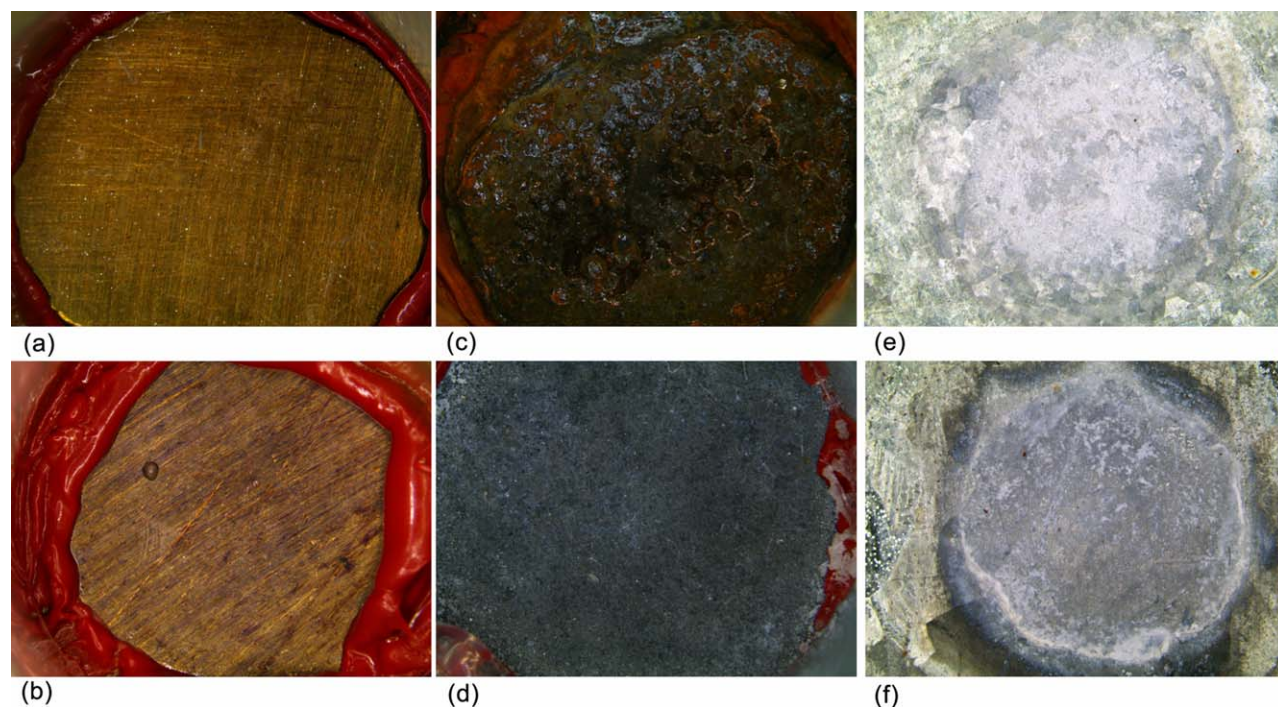


**Figure 9.** SEM images of the residual wear patterns: (a) polysiloxane coating alone and (b) VTEOS interlayer + polysiloxane coating.

Aforementioned considerations are supported by the examination of SEM images (Figure 9) of the residual wear pattern after intermediate sliding distance (i.e., 200 m). Damage observed on coatings involving VTEOS interlayers is more uniform as result of the better overall chemical structure of these coatings. Differently, the coatings involving the polysiloxane resin alone show a major fragmentation of the structure after 200 m sliding distance. This phenomenon could be more likely ascribed to the different chemical arrangement of these coatings.

#### Analysis of the Chemical Endurance

The resistance of selected substrates to aggressive chemicals depends on several factors: (i) interfacial adhesion between coating and substrate; (ii) coating thickness; and (iii) coating structure and its eventual defectiveness.<sup>22–25</sup> Salt, acidic, and, in particular, alkaline environments are detrimental to the endurance of metal substrates. Organic coatings often fail in protecting the underlying metal substrate as their ability to barrier the aggressive chemicals is counterbalanced by their limited



**Figure 10.** Maximum extent of corrosion damage before failure after exposure of the coatings with the salty (NaCl 5 wt %) solution: (a) polysiloxane coating alone, after 154 h; (b) VTEOS interlayer + polysiloxane coating, after 154 h; (c) as-received Fe 430 B substrate, after 26 h; (d) Zn-coated Fe 430 B by cold spraying, after 90 h; (e) Zn-coated Fe 430 B by electro-galvanizing, after 90 h; and (f) Zn-coated Fe 430 B by hot dipping, after 26 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table III.** Response of the Investigated Coating System Against Salty, Acidic, and Alkaline Environments

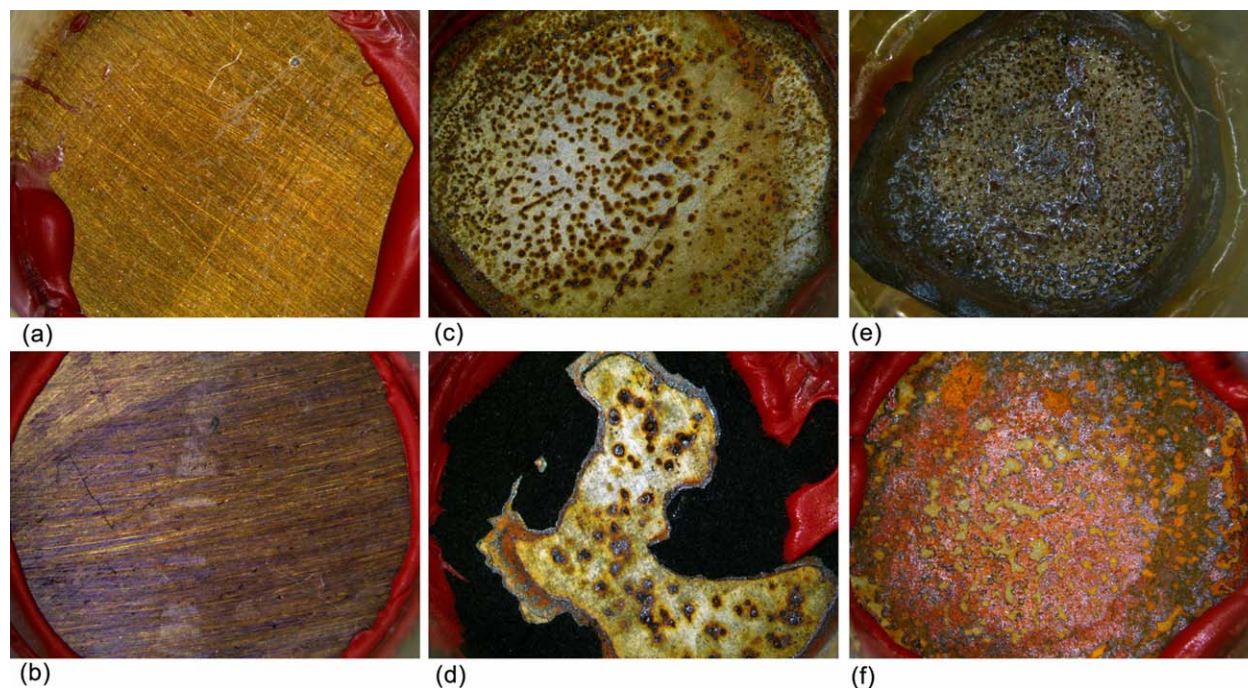
	Exposure time (h)					
	2	5	11	26	90	154
<b>NaCl (5 wt %) salty environments</b>						
Polysiloxane alone	-	-	-	-	-	-
Vinyltriethoxysilane + polysiloxane	-	-	-	-	-	-
As-received Fe 430 B	Onset	Serious	Severe	Severe	Fail	-
Zn coated Fe 430 B (electro-galvanizing)	Onset	Onset	Onset	Onset	Serious	Fail
Zn coated Fe 430 B (cold spraying)	Onset	Serious	Serious	Severe	Severe	Fail
Zn coated Fe 430 B (hot dipping)	Onset	Fair	Fair	Serious	Fail	-
<b>HCl (5 wt %) acidic environments</b>						
Polysiloxane alone	-	-	-	-	-	-
Vinyltriethoxysilane + polysiloxane	-	-	-	-	-	-
As-received Fe 430 B	Onset	Serious	Serious	Severe	Fail	-
Zn coated Fe 430 B (electro-galvanizing)	Onset	Serious	Serious	Severe	Fail	-
Zn coated Fe 430 B (cold spraying)	Onset	Fail	-	-	-	-
Zn coated Fe 430 B (hot dipping)	Onset	Serious	Serious	Severe	Fail	-
<b>NaOH (5 wt %) alkaline environments</b>						
Polysiloxane alone	-	-	-	-	-	-
Vinyltriethoxysilane + polysiloxane	-	-	-	-	-	-
As-received Fe 430 B	Onset	Serious	Fail	-	-	-
Zn coated Fe 430 B (electro-galvanizing)	Onset	Onset	Fail	-	-	-
Zn coated Fe 430 B (cold spraying)	Onset	Onset	Fail	-	-	-
Zn coated Fe 430 B (hot dipping)	Onset	Onset	Fail	-	-	-

Onset = activation of corrosion damage; Fair = first propagation of corrosion damage; Serious = extended propagation of corrosion damage; Severe = corrosion damage covers more than the half of the exposed surface; Fail = rupture of the coatings or uncontrolled spreading of corrosion damage.

interfacial adhesion (i.e., only gluing by mechanical interlocking with the metal surface<sup>26</sup>). Limited adhesion is surpassed in this work, using functionalized polysiloxane resin with hydroxyl and alkoxy groups or combination of VTEOS interlayer with an overlaying coating with the same functionalized polysiloxane resin. As said before, in both cases the interfacial adhesion is ensured by the covalent bonds between the hydroxyl groups on the metal surface with the corresponding counterparts (hydroxyl and/or alkoxy groups) on VTEOS and functionalized methyl phenyl polysiloxane resin. However, several studies reported in the literature referred how coatings made from hybrid organic-inorganic resin or thin organo-silane layers could offer limited protection to the underlying metal in spite of their potentially good adhesion.<sup>8–11,27</sup> Prehydrolyzed organo-silane layers were also found to fail as a result of their brittleness and long time exposure to aggressive chemicals cause their fragile rupture.<sup>8</sup> Epoxy modified polysiloxane resin were found to ensure improved protection as their increased ductility and good barrier properties. However, the attempt to find a good compromise between the chemical affinity of the resin with the metal and its ductility and flexibility took to hybrid designs insufficient to withstand in many aggressive environments (for example, in alkaline solutions). Despite the good barrier ability of

the hybrid epoxy-polysiloxane coatings, their limited mechanical properties (i.e., softness) and just fair adhesion to the substrate allowed the infiltration of corrosive products at interface with the metal and, concurrently, the failure of the protection system.<sup>9</sup> Combination of silane-based ((3-glycidoxypropyl)methyl-diethoxysilane<sup>10</sup> or vinyltriethoxysilane<sup>11</sup>) interlayers with overlying purely organic layers (i.e., epoxy coatings) were found to offer the best protection to aggressive chemicals, although alkaline solutions were still found to easily interact with the substrate by infiltration and cause bulging and fracture of the coating systems.<sup>10,11,27</sup> Coatings based on the functionalized methyl phenyl polysiloxane resin and double-layers of VTEOS interlayer and functionalized methyl phenyl polysiloxane resin displayed improved performance and utmost resistance to chemical attacks with aggressive salty (NaCl 5 wt %), acidic (HCl 5 wt %), and alkaline (NaOH 5 wt %) solutions. The investigated coatings offer comparable protections to the underlying Fe 430 B substrates when dipped under salty solutions, and they were unaffected even after the longest exposure time of 154 h (Figure 10). All the reference samples (uncoated Fe 430 B, Zn coated Fe 430 B by cold deposition, hot dipping and electro-galvanizing processes) failed (Table III). In particular, the samples zinc coated by cold spraying and hot dipping showed the



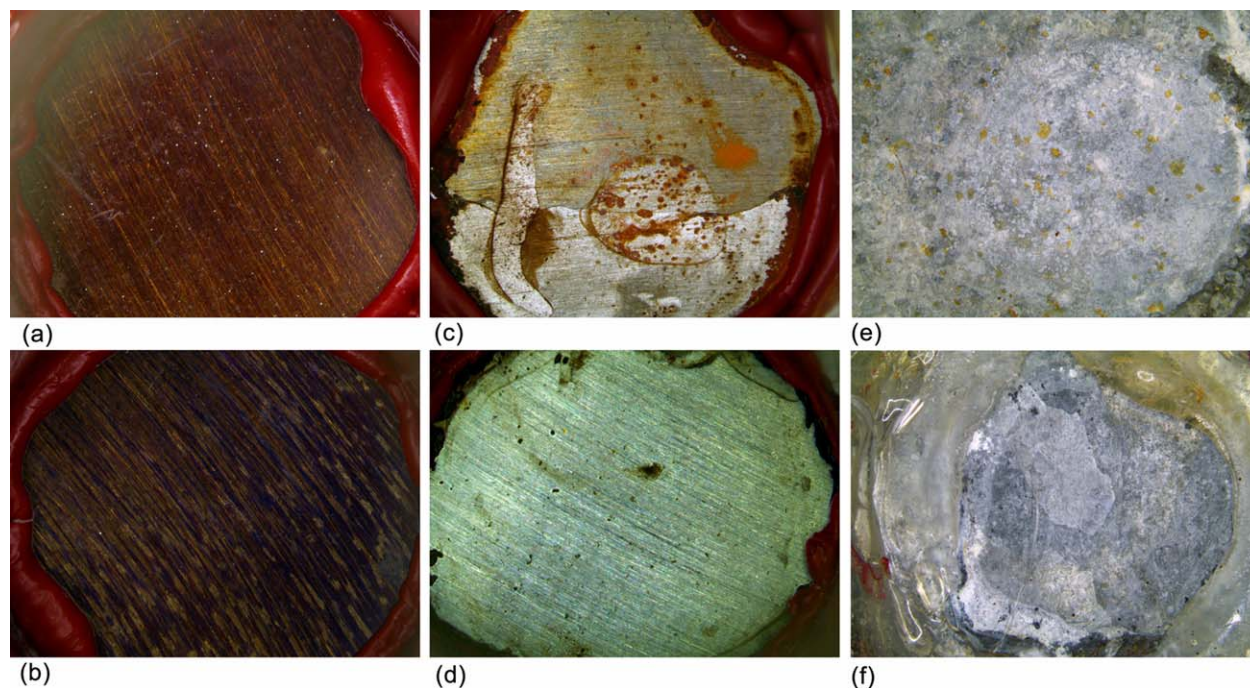


**Figure 11.** Maximum extent of corrosion damage before failure after exposure of the coatings with the salty (HCl 5 wt %) solution: (a) polysiloxane coating alone, after 154 h; (b) VTEOS interlayer + polysiloxane coating, after 154 h; (c) as-received Fe 430 B substrate, after 26 h; (d) Zn-coated Fe 430 B by cold spraying, after 2 h; (e) Zn-coated Fe 430 B by electro-galvanizing, after 26 h; and (f) Zn-coated Fe 430 B by hot dipping, after 26 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

onset of corrosion after 2 h. Failure took place after 90 h. The sample zinc coated by electro-galvanizing showed the onset of corrosion damage after 90 h to fail after 154 h. In acidic environment (Figure 11), the polysiloxane coatings alone and the coating system composed by VTEOS interlayer and polysiloxane coatings withstand the whole test duration (154 h). In contrast, the corrosion damage spread quickly on all the Zn coated samples (Table III). The damage onset took place after only 2 h exposure time. The sample zinc coated by cold processing failed after only 5 h. The samples zinc coated by hot dipping and electro-galvanizing underwent major damage after only 5 h. Complete failures occurred after 90 h. Failure of zinc protection in salty and acidic environments can be ascribed to the chemical attack of the aggressive ions at the surface of the coating. Pitting followed by severe fracturing compromised quickly the Zn coatings performance, thus leading to their early failure. In alkaline environments (Figure 12), the polysiloxane coatings alone and the system VTEOS + polysiloxane coating withstands the whole test duration (154 h). In contrast, the Zn coated samples were all found to fail after only 11 h exposure time. Failure of Zn coated samples occurred by infiltration of the alkaline species at the interface metal-Zn. Zn coatings were quickly bulged and, concurrently, early failure took place.

The results of the dipping tests of the coated Fe 430 B samples in aggressive salty, acidic, and alkaline solutions show the potentiality of the methyl phenyl polysiloxane coatings and their combination with organo-silane interlayers. Such systems were found to offer unprecedented protection against

aggressive chemicals, better than Zn coated systems and, based on the data available in the literature,<sup>10,11,27</sup> even better than hybrid epoxy-polysiloxane coatings. Improved performance of methyl phenyl polysiloxane can be more likely ascribed to the intrinsic resin structure. Organic functionalization is made from nonreactive and small lateral methyl and phenyl groups, which contribute to make flexible the resin structure without significantly compromising its capability to react with the functional groups on metals and organo-silane interlayers. Similarly, hydroxyl and alkoxy groups located on the side chains are still reactive enough and not too much hindered by the steric hindrance of the long polysiloxane chains to combine with their counterparts on metals and interlayers to form solid covalent bonds. Therefore, the good mechanical properties offered by the polysiloxane resin, that is the result of the good compromise between the ductility ensured by the lateral methyl and phenyl groups and stiffness of the Si—O backbones, combined with the utmost adhesion at the metal and interlayer interface can be inferred as the leading reasons for the outstanding chemical resistance shown by the resulting coating systems. Although there are no visible difference after 154 h against salty, acidic, and alkaline solutions between polysiloxane and VTEOS/polysiloxane coatings in terms of their chemical performance, VTEOS interlayers are extremely useful as they consolidate the covalent bond between coating and metal at the interface and increase the mechanical response. This is of utmost interest as in the industrial practice, coated steels must withstand concurrent erosion–corrosion and



**Figure 12.** Maximum extent of corrosion damage before failure after exposure of the coatings with the salty (NaOH 5 wt %) solution: (a) polysiloxane coating alone, after 154 h; (b) VTEOS interlayer + polysiloxane coating, after 154 h; (c) as-received Fe 430 B substrate, after 5 h; (d) Zn-coated Fe 430 B by cold spraying, after 5 h; (e) Zn-coated Fe 430 B by electro-galvanizing, after 5 h; and (f) Zn-coated Fe 430 B by hot dipping, after 5 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

superior mechanical response means enhanced response to combined erosion–corrosion attacks.

## CONCLUSIONS

The manufacturing of methyl phenyl polysiloxane and VTEOS + methyl phenyl polysiloxane coatings on Fe 430 B substrates is the topic of the present investigation. The coating process is simple and consists in the spraying of diluted solutions. Prehydrolysis is only required for the preparation of the VTEOS interlayer.

The coatings were tested for visual appearance, micromechanical and tribological response as well as for chemical endurance against aggressive salty, acidic, and alkaline solutions. The following results can be summarized:

- The manufacturing process generates aesthetic coatings with simple, cheap, and environmental sustainable operations. Such process can be a valid and low cost alternative to the more expensive, energy consuming, and pollutant zinc deposition process, especially the electro-galvanizing;
- The thickness of the coatings, crucial for the grade of protection they can provide, is approximately 60–70  $\mu\text{m}$  thick, that is, comparable with the typical thickness of Zn layers commonly used in the industrial practice;
- Scratch and wear resistance of the functionalized polysiloxane and VTEOS + polysiloxane coatings is good and depends on the chemical structure of the system. In particular, the highly reactive VTEOS bonds better with both metal and hydroxyl

and alkoxy functionalized methyl phenyl polysiloxane, thus ensuring improved mechanical response;

- The functionalized polysiloxane and VTEOS + polysiloxane coatings show outstanding performance when their chemical endurance is tested by dipping in salty, acidic, and alkaline environments. They can easily withstand 1 week under a continuous exposure to salty, acidic, and alkaline concentrated solutions without any onset of corrosion damage. Comparative zinc coated Fe 430 B substrates fail in short order and reveal a particular weakness against acidic and, even more, alkaline environments.

In conclusion, the chemical protection offered by the functionalized polysiloxane and VTEOS + polysiloxane coatings are superior to competitive systems (e.g., bilayer of functional organo-silanes with epoxy functionalized polysiloxane topcoat) reported in the literature. Therefore, the utmost protection grade the coatings are able to ensure together with the reliability of the manufacturing process guarantee a high potential of the investigated spraying technology in many industrial segments.

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