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Novel, Water-Based High-Performance Primers That Can Replace Metal Pretreatments and Chromate-Containing Primers

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In previous research it was demonstrated that simple rinses with organofunctional silanes can be used to protect metals against various forms of corrosion. Such treatments also improve paint adhesion. However, when unpainted, the silane films are too thin to provide long-term corrosion protection. In this paper it will be shown that much thicker, primer-like coatings can be obtained from silanes if the silanes are mixed with organic resins and small particles, preferably nanosize. Self-priming coatings of up to 20 µm in thickness have been obtained with outstanding adhesion and corrosion protection properties. The components of such "superprimer" systems are all water-based, and they do not contain chromates or other toxic ingredients. Thus, they are environmentally friendly. This paper describes several successful superprimers and presents their performance data.

Keywords chromate-free coatings, organofunctional silanes, self-priming coatings, superprimer

1. Introduction

Organofunctional silanes have been shown to protect various metal substrates from different types of corrosion. These treatments have been known to improve paint adhesion, too. A usual thickness for a silane film is around 200-500 nm. Such a thin film is incapable of providing long-term corrosion protection without the presence of a topcoat over the silane pretreated metal substrate. Mechanical abrasion can also destroy these thin silane films. This problem has been dealt with through the addition of inorganic and organic inhibitors to the silane film. These inhibitors can leach out and prevent the metal substrate from corroding.[1-5] However, a self-priming coating, i.e., "superprimer," on the order of 20 µm thickness can be obtained by using organofunctional silanes as the curing agent with a resin. Polyurethane was used for this purpose in this research. The resultant coatings were found to be very robust and demonstrated excellent corrosion resistance.

Organofunctional silanes crosslink the polyurethane in the same way as commonly used amine-containing curing agents. The conventional primers contain chromate, which have Cr (VI) ions. Cr (VI) ions are toxic and carcinogenic.[5] As such, the scientific community is looking for a replacement, and self-priming "superprimer" coatings offer a good alternate to the current pretreatment processes and chromate-containing primers.

2. Mechanism

The general structure of organofunctional silanes is shown in Fig. 1. A superprimer can be prepared with these organofunctional silanes when the silanes are mixed with water-soluble epoxy, polyester, polyurethane, or acrylate resins. The mixture comprises 30-40 vol.% silane and resin. Silanes have been added to paints for better corrosion resistance and as a pretreatment for particles added to the paints. However, the amount of silane added was typically below 10.

Metal oxides can also be added to the mixture. Some examples of metal oxides that can be added to the "superprimer" include zinc oxide, titanium dioxide, silica, and alumina. The quantity of these additives is about 10%. Further, around 1 vol.% of other additives such as surfactants, thickeners, ultraviolet (UV) absorbers, and inhibitors can also be incorporated in the coating.

The polymer backbone is crosslinked with the silane, as

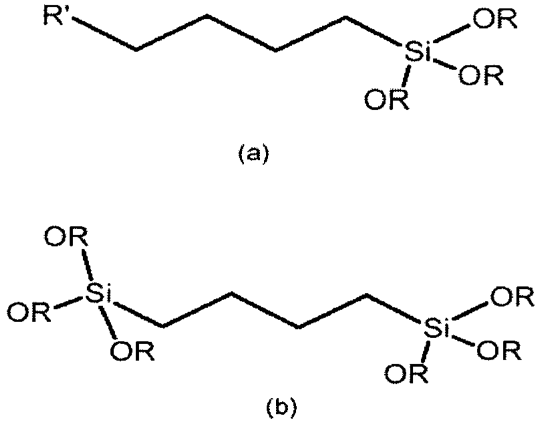

Fig. 1 Structure of organfunctional silanes: **(a)** mono-Silane **(b)** bis-silane

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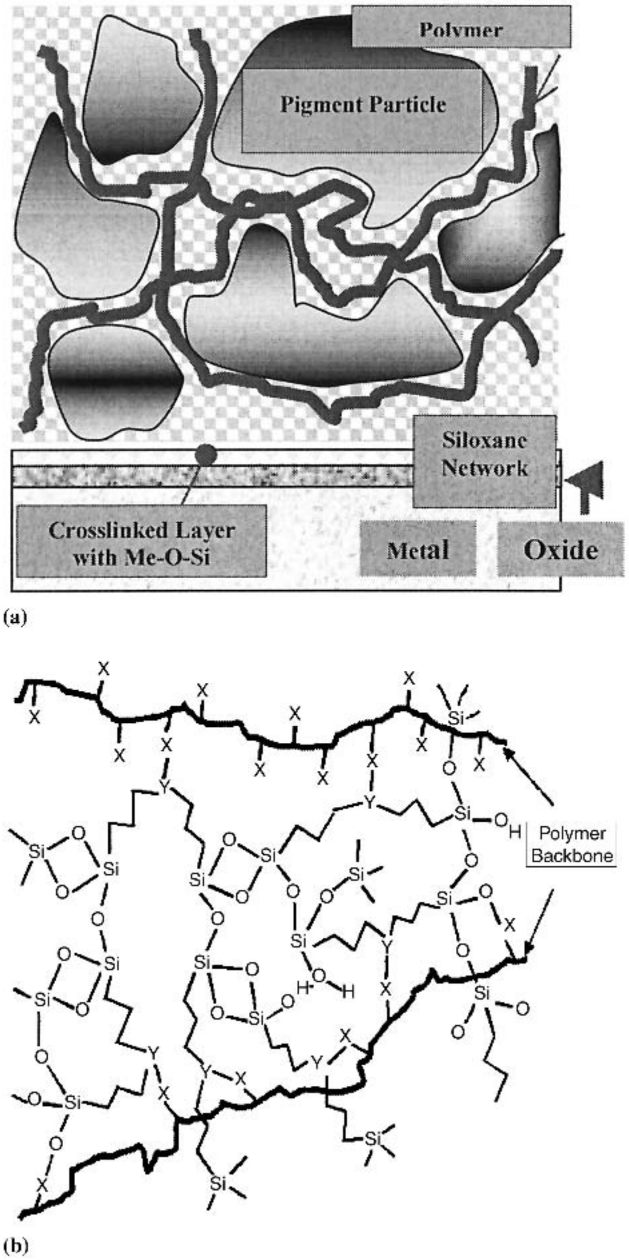
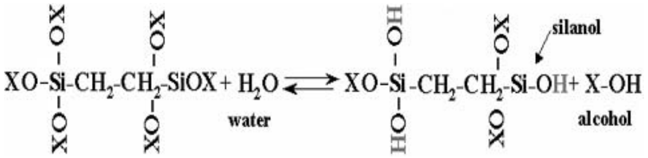


Fig. 2 **(a)** Schematic representation of formation of superprimer coating on metal substrate and **(b)** schematic representation of crosslinking in a superprimer coating on the polymer backbone

shown in Fig. 2. The organofunctional silanes are hydrolyzed with the water present in the superprimer and result in the presence of silanol groups in the superprimer. The reaction mechanism of hydrolysis for the silanes is represented in Fig. 3.

The silanol group bonds with the metal substrate, as shown in Fig. 4. The Me-O-Si bonds are formed, and above that a siloxane network is present. The presence of a resin with the organofunctional silanes causes the polymer backbone to be embedded in the siloxane network. The resultant network is represented in Fig. 2(b). This method causes the coating to have a thickness on the order of 20 μm. The presence of the polymer backbone also increases the resistance of the film to mechanical abrasion.



$$\mathrm{XO\text{-}\overset{OX}{\underset{OX}{Si}}\text{-}CH_2\text{-}CH_2\text{-}\overset{OX}{\underset{OX}{Si}}OX + H_2O \rightleftharpoons XO\text{-}\overset{OH}{\underset{OH}{Si}}\text{-}CH_2\text{-}CH_2\text{-}\overset{OX}{\underset{OX}{Si}}\text{-}OH + X\text{-}OH}$$

Fig. 3 Mechanism of hydrolysis for silanes

3. Experimental

3.1 Materials

3.1.1 Substrate. For the purpose of this research, the metal substrate chosen was cold-rolled steel. Panels were procured from A.K. Steel (Middletown, OH).

3.1.2 Polyurethane. Polyurethane PU 402 A was obtained from the Bayer Group (Pittsburgh, PA).

3.1.3 Silanes. Silanes were procured from Gilest (Morrisville, PA). Three silanes were investigated for this research. First, WSA-7011-100GM (60-75% aminopropyl silsequioxane)-(25-35% methyl silsequioxane) copolymer (referred to as AMME). The second was WSAV-6511-100GM (60-65% aminopropyl silsequioxane)-(35-40% vinyl silsequioxane) (referred to as AMVS). A third silane, A 19201, which contains a suspension of alumina, was also investigated. This silane was procured from Chemat, Inc.

3.2 Procedures

3.2.1 Sample Cleaning. The panels were cleaned to remove the mill dust and grease on the surface. This process was done by ultrasonic cleaning in solutions of n-hexane followed by acetone and ethyl alcohol. These panels were then subjected to alkaline cleaning at 60-65 °C for 7 min. The alkaline cleaner was procured from OSi Chemicals (South Charleston, WV).

3.2.2 "Superprimer" Preparation. The "superprimer" was prepared by mixing polyurethane PU 402 A and silane with the other additives in a beaker in the desired ratios and stirring it at a high shear rate. This solution was held for 15-20 min before using it for coating the panels so that crosslinking between the polymer backbone and the silane molecules could occur.

3.2.3 Coating Application. The coatings were made using a draw-down bar of number R14. The coated panels were cured at 120 °C for various times to investigate the effect of cure duration on coating performance. The coatings can also be applied by alternate methods, such as brushing, wiping, roll coating, or dipping.

3.3 Testing

3.3.1 Electrochemical Impedance Spectroscopy (EIS). Electrochemical impedance spectroscopy (EIS) was used as a technique to evaluate the performance of the coatings. These tests were conducted in a 0.6 *M* NaCl (pH 6.5) aqueous solution, using a SR 810 frequency-response analyzer and a

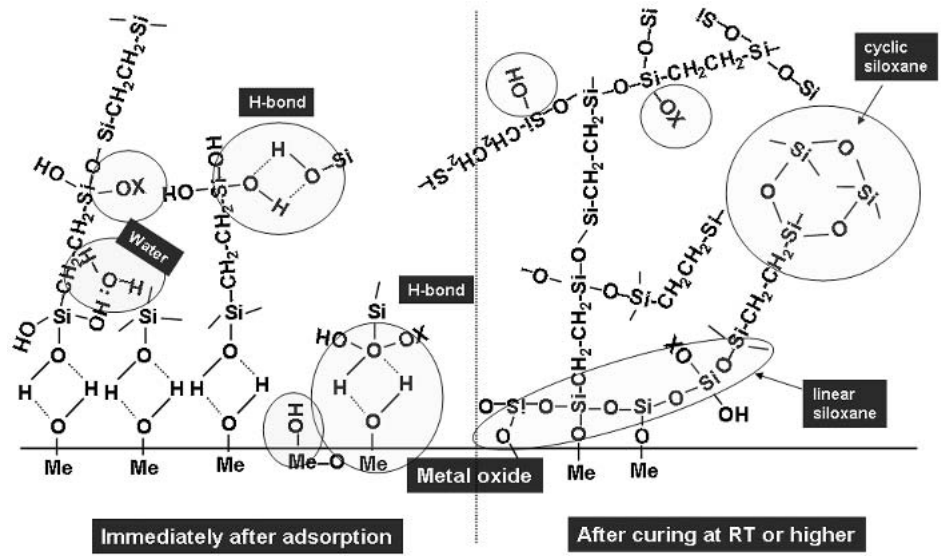


Fig. 4 Hydrolysis, condensation, and adsorption of a silane film on a metal substrate. Note the Me-O-Si bonds formed after curing at room temperature or elevated temperatures.

Gamry (Gamry Instruments, Warminster, PA) CMS 100 potentiostat. Impedance data were recorded at frequencies ranging from 10^{-2} to 10^5 Hz, with alternating current (ac) voltage amplitude of ±10 mV. A commercial saturated calomel electrode (SCE) served as the reference electrode, coupled with a graphite counter electrode. An area of 3.14 cm^2 was exposed to the electrolyte during measurements.

3.3.2 Saltwater Immersion Testing. Strips from the panels were bent in a U-shape, with the coated surface facing the concave side. These strips were immersed in a 0.6 *M* NaCl (pH 6.5) aqueous salt solution.

4. Results and Discussion

Table 1 shows the various superprimer coatings that were investigated for their corrosion resistance performance.

4.1 Electrochemical Impedance Spectroscopy Testing

Electrochemical impedance spectroscopy was conducted on all panels after exposure for 24 h to the electrolyte. The results of the spectroscopy are shown in Fig. 5-8.

The log modulus of the resistance observed at lower frequencies can be compared for all the superprimer coatings. The comparison suggests that the coatings numbered 1, 3, 5, and 8 resulted in the best barrier to corrosion and the best barrier to the penetration of the electrolyte through the film.

For the WSA-7011-100GM (60-75% aminopropyl silsequioxane)-(25-35% methyl silsequioxane) solution, the data indicate that as the amount of copolymer is increased, the superprimer performance improves dramatically.

Also noteworthy is the fact that the presence of vinyl groups in the superprimer coating made with WSAV-6511-100GM (60-65% aminopropyl silsequioxane)-(35-40% vinyl silsequioxane) gives log modulus of resistance equivalent to the other coatings, despite the fact that coating had been further diluted with water.

Table 1 Formulations of Superprimers Coatings

Coat No.	PU 402 A, mL	AMME Silane, mL	A 19201 (Chemat Silane), mL	AMVS Silane, mL	Water, mL
Cntrl	100	…	…	…	…
1	60	10	30	…	…
2	70	30	…	…	…
3	67.5	32.5	…	…	…
4	50	…	50	…	…
5	70	…	30	…	…
6	60	10	10	…	…
7	50	20	…	…	30
8	44.44	…	…	33.33	22.23

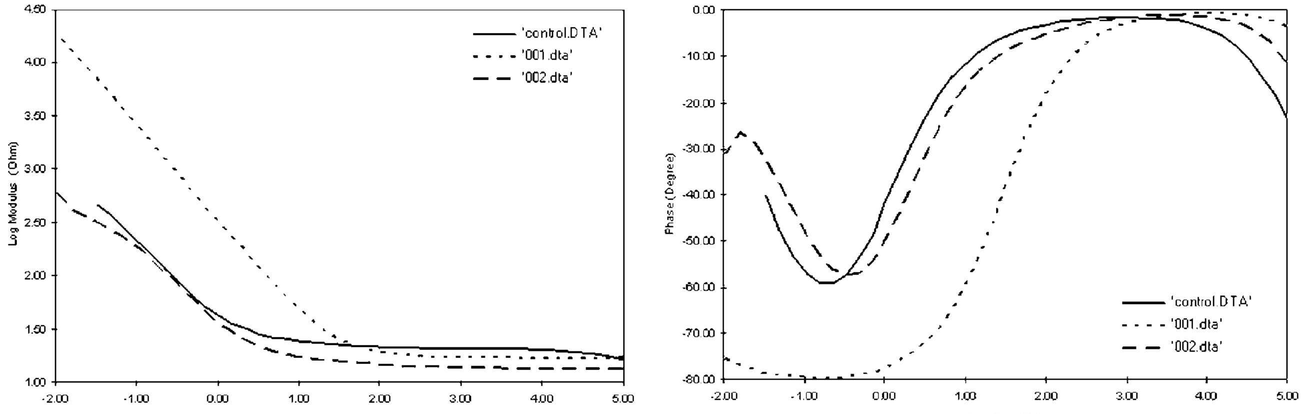
All the panels were cured at 120 °C for 10 min.

4.2 Effect of Varying Time of Curing

The previous results suggest that vinyl groups in the silane make the coating more hydrophobic. This concept was investigated by comparing superprimer coatings made with both the silanes. The first set of coatings were made with the WSA-7011-100GM (60-75% aminopropyl silsequioxane)-(25-35% methyl silsequioxane) copolymer and PU 402 A polyurethane, in the ratio 32.5:67.5. The second set of coatings was made with WSAV-6511-100GM (60-65% aminopropyl silsequioxane)-(35-40% vinyl silsequioxane) and PU 402 A polyurethane, in the same ratio. A set of coatings was also made by first pretreating the metal substrate with WSAV-6511-100GM (60-65% aminopropyl silsequioxane)-(35-40% vinyl silsequioxane), followed by a topcoat of PU 402 A. Coatings for each were cured at 120 °C for 10, 30, and 60 min. Table 2 describes the sample numbering nomenclature.

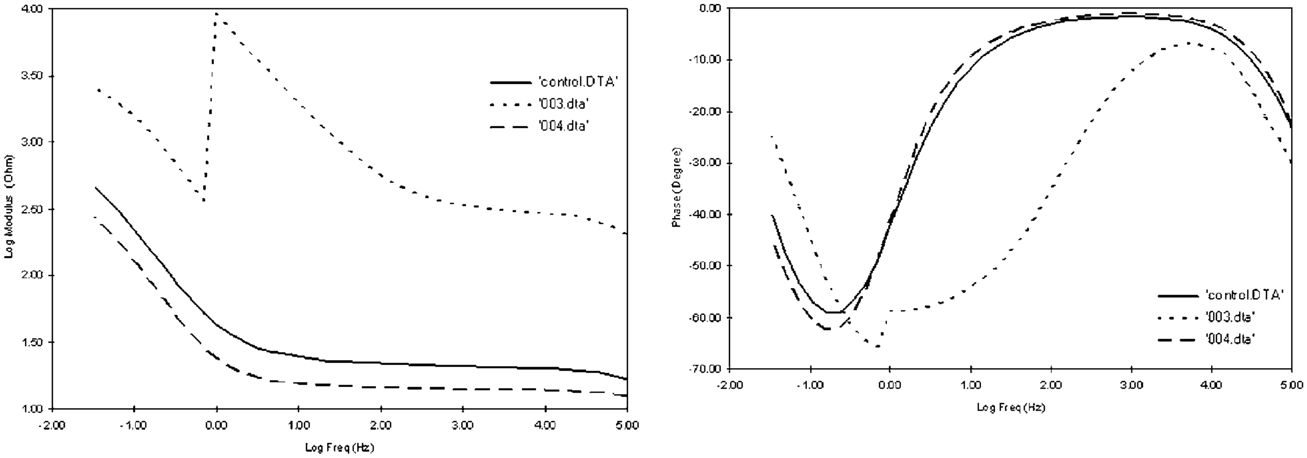
The effect of curing time is observed in the EIS data shown in Fig. 9-11.

The Bode plots show that for the WSAV-6511-100GM (60-65% aminopropyl silsequioxane)-(35-40% vinyl silsequioxane)



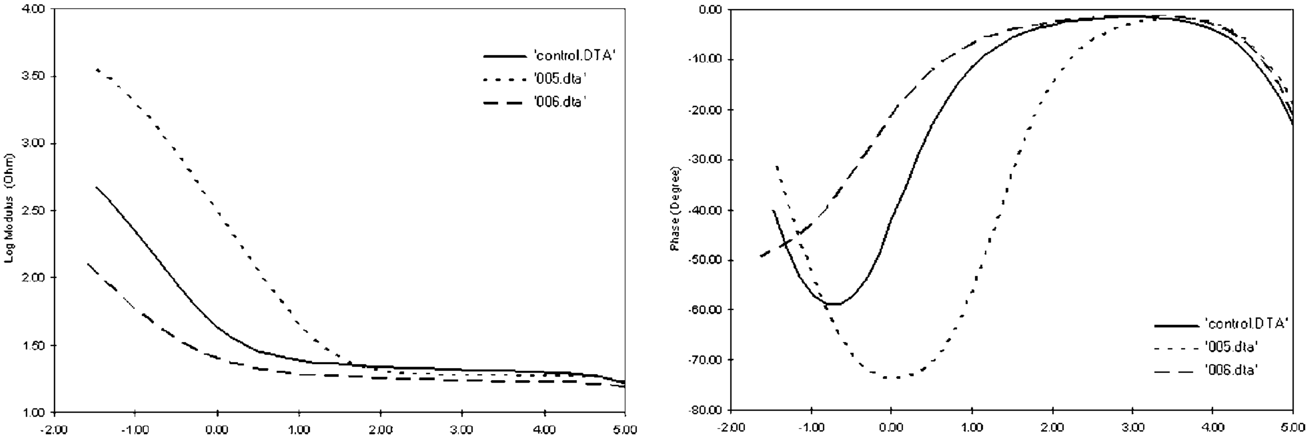
(a) (b)

Fig. 5 Electrochemical impedance spectroscopy data after 24 h of exposure to electrolyte for coatings 1 and 2, compared with the control sample



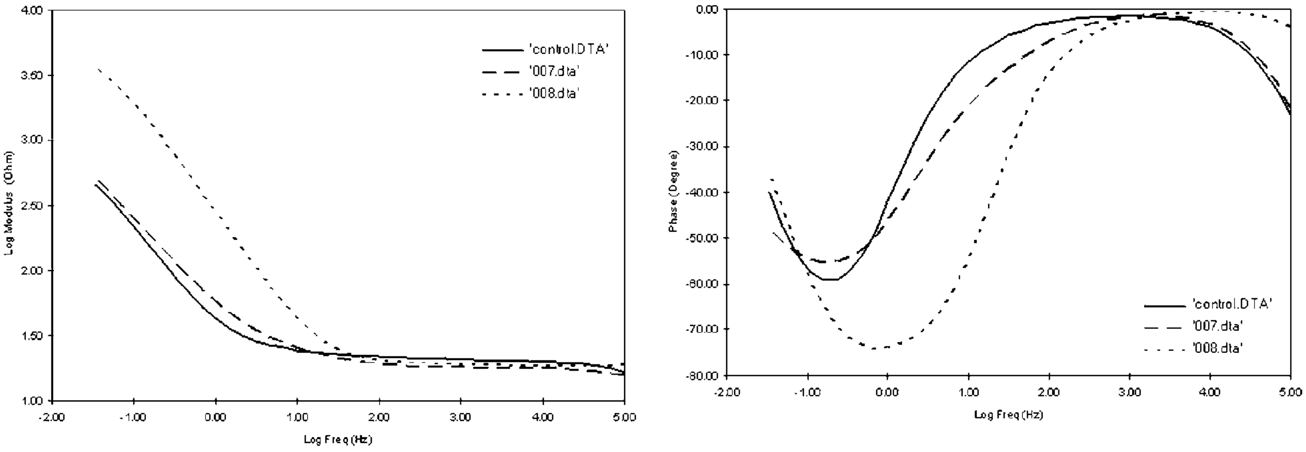
(a) (b)

Fig. 6 Electrochemical impedance spectroscopy data after 24 h of exposure to electrolyte for coatings 3 and 4, compared with the control sample



(a) (b)

Fig. 7 Electrochemical impedance spectroscopy data after 24 h of exposure to electrolyte for coatings 5 and 6, compared with the control sample



(a) **(b)**

Fig. 8 Electrochemical impedance spectroscopy data after 24 h of exposure to electrolyte for coatings 7 and 8, compared with the control sample

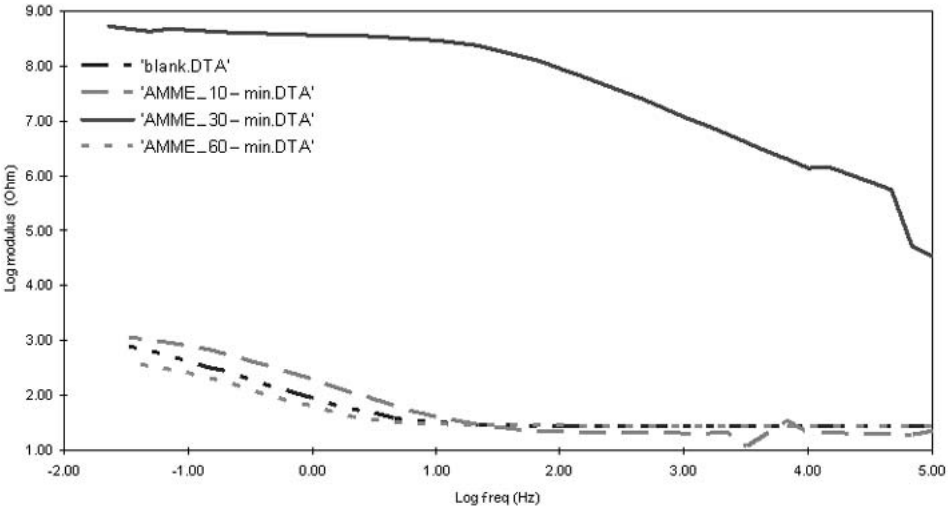


Fig. 9 Comparison of EIS plots for superprimer (PU 402 A: AMME:: 67.5:32.5) to show effect of curing duration

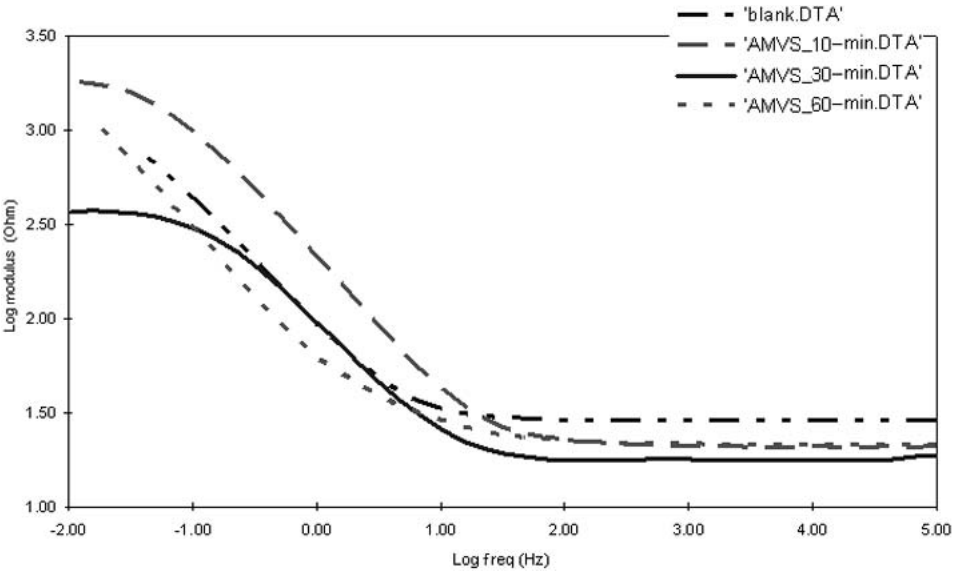


Fig. 10 Comparison of EIS plots for superprimer (PU 402 A: AMVS:: 67.5:32.5) to show effect of curing duration

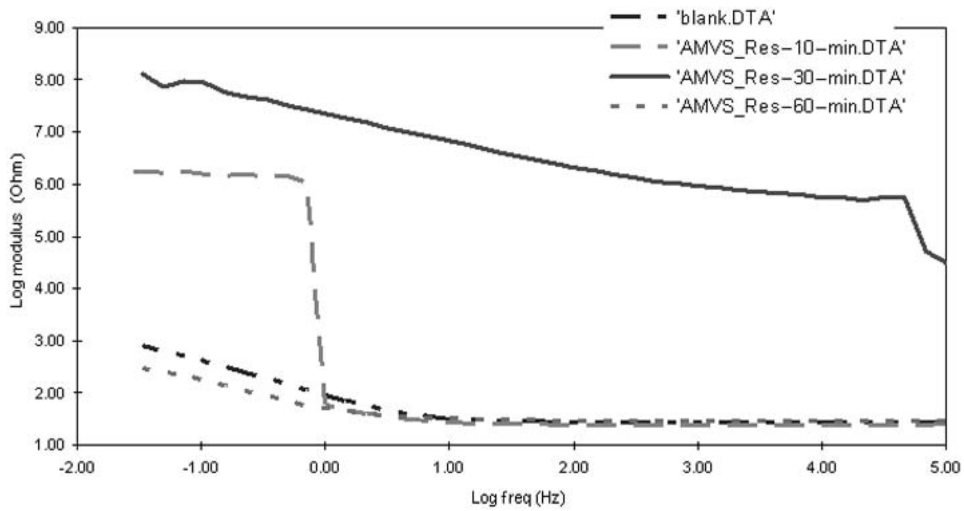


Fig. 11 Comparison of EIS plots for superprimer (AMVS pretreatment followed by PU 402 A topcoat) to show effect of curing duration

Table 2 Nomenclature for Sample Naming

Serial No.	Sample Name	Coating Formulation	Curing Time, min
1	Blank	PU 402 A	10
2	AMME_10min	PU402A/AMME 67.5:32.5	10
3	AMME_30min	PU402A/AMME 67.5:32.5	30
4	AMME_60min	PU402A/AMME 67.5:32.5	60
5	AMVS_10min	PU402A/AMVS 67.5:32.5	10
6	AMVS_30min	PU402A/AMVS 67.5:32.5	30
7	AMVS_60min	PU402A/AMVS 67.5:32.5	60
8	AMVS_Res_10min	AMVS pretreatment with a topcoat of PU 402 A	10
9	AMVS_Res_30min	AMVS pretreatment with a topcoat of PU 402 A	30
	AMVS_Res_60min	AMVS pretreatment with a topcoat of PU 402 A	60

Table 3 Ranking of Performance of U-Shaped Strips Coated with Superprimer after 24 h of 0.6 *M* NaCl Aqueous Solution Exposure

Coating	Ranking as per Extent of Rusting Observed (1 Means Most Rusted, 9 Means Least)	Peeling Observed, if any, with Comments
Control	6	No peeling observed, though very tiny blisters seen.
1	9	Coating seen to peel at the edge on the top, but no significant rusting observed in the sample.
2	4	No peeling on bent surfaces but away from it on edges of coating.
3	3	Peeling occurs on the area of bend and other areas, too.
4	7	A very little amount of peeling at the area of bend observed, otherwise film fairly intact.
5	8	No peeling on bent surface, but away from it on edges of coating.
6	5	Blistering in increasing magnitude observed while moving away from the area of bend. No significant rusting seen.
7	1	Four spots of peeling observed at the area of bend.
8	2	Peeling observed over the bent area.

based coatings, a 30 min curing time is best. For the WSA-7011-100GM (60-75% aminopropyl silsequioxane)-(25-35% methyl silsequioxane) copolymer-based coatings, a 10 min curing time is optimum. As the temperature is increased above the optimum temperature, it is seen that the log modulus of resistance for the lower frequencies decreases.

4.3 Saltwater Immersion Testing

Strips from coated samples, as listed in Table 1, were bent into a U-shape to approximate a Mandrill test. These samples were inspected after 24 h of immersion in 0.6 *M* NaCl aqueous solution for deterioration of the coating. Coating performance was evaluated.

The results are described in Table 3. As seen, the formulation of PU 402 A with WSA-7011-100GM (60-75% aminopropyl silsequioxane)-(25-35% methyl silsequioxane) copolymer was found to perform well.

EIS spots of the area exposed to the electrolyte for four days on the panel are shown in Fig. 12. These spots also suggest that the formulation was the best from among the ones tested.

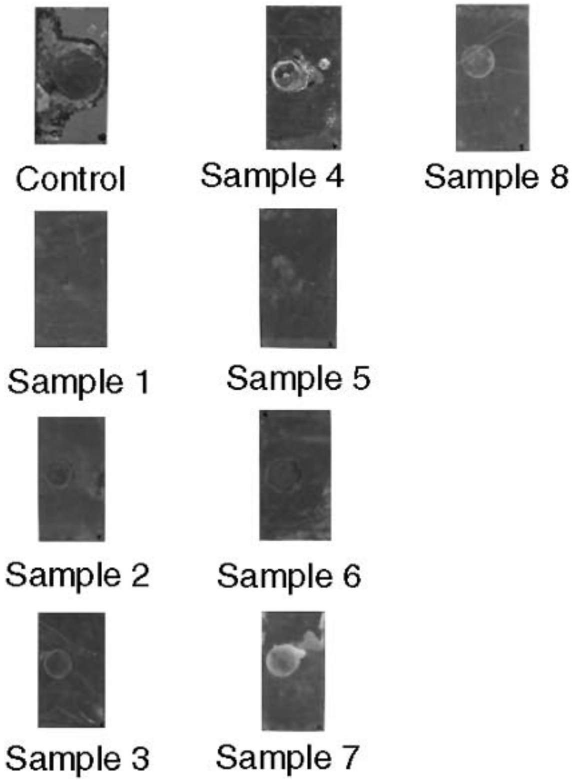


Fig. 12 Images of electrochemical impedance spectroscopy spots after four days of electrolyte exposure

5. Conclusions

This study confirms the potential of superprimer coatings as a replacement for chromate-containing primers. These self-priming coatings do not contain any toxic or carcinogenic components. Also these coatings are water based and easy to make. These advantages, coupled with the excellent corrosion protection, make them an excellent alternate for the current chromate-containing primers and offset the disadvantages of the bare organofunctional silane films.

Further research is needed to study the performance of these coatings with additives. Self-healing properties, typical to the chromate pretreatment, have been incorporated in the bare organofunctional silane films.[5] The effect of addition of such pigments to the superprimer also needs to be investigated.

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