

Effect of Pre-Hydrolyzed Tertaethoxysilane Addition in Organic-Inorganic Films Applied on Aluminium Alloy

Gopal Chawada and Bharatkumar Z Dholakiya

Department of Chemistry, S.V. National Institute of Technology, Surat, Gujarat

Email: bharat281173@gmail.com

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Abstract: Sol-gel derived organic-inorganic hybrid (OIH) coatings have emerged as efficient and environmentally-friendly alternatives to hazardous chromate-based systems used in metal finishing industry. The thin OIH films derived from organo-silane precursors can be used as very effective pretreatment for aluminum alloys to improve corrosion resistance. The OIH coating performance can be effectively manipulated, at micro and nano scales, by choice of sol-gel precursor, bath composition, pH, and processing conditions, among other factors. In the present work, a bis-silane compound has been prepared by reaction of liquid epoxy resin with amino-silane compound and used as a primary sol-gel precursor in conjunction with tetraethoxyorthosilane (TEOS). OIH coatings with varying TEOS content have been deposited on an aluminum alloy substrate (Al 2024-T3). The corrosion resistance has been studied using salt spray technique. The study shows that optimum film performance can be obtained by choice of precursor composition and processing conditions.

Keywords: Sol-gel, OIH, Aluminum Alloy, Salt Spray.

1. Introduction

Aluminum alloys, such as AA2024-T3, are widely used in structural applications requiring high strength to weight ratio, as well as good fatigue resistance. such as in aerospace, automobile, and military related applications. These materials, however, are very susceptible to oxidation and corrosion when exposed to environment, particularly in chloride containing atmosphere¹⁻³. For protection of aluminum alloys from environmental corrosion it is common practice to apply multi-coat protective coating system consisting of a conversion coating (pretreatment), a primer and a top-coat⁴. The pretreatment, which is applied directly on the bare metal surface, is very critical to success of the entire system since its primary role is to provide

corrosion resistance and to provide excellent adhesion of the subsequent primer coat⁵.

One of the most efficient pretreatments for aluminum alloys are chromate conversion coatings deposited from a tri and hexavalent chromium salt solution by reaction with aluminum. Such conversion coatings not only have excellent passive corrosion resistance but also provide “self-healing” properties due to the presence of residual Cr (VI) ions that can migrate to the damaged area and repairs the damage. However, Cr (VI) due to its carcinogenic and toxic nature poses serious health and environmental challenges, and therefore has been subject to severe government regulations^{6,7}. Therefore, there has been tremendous interest in the development of alternative sustainable *chromate-free* pretreatment systems that are environmentally friendly and efficient.

Among many different chromate-free pretreatment systems, coatings deposited by sol-gel process have been found very promising. Silane-based organic-inorganic hybrid sol-gel coatings are currently used as pre-treatment for various metallic substrates, such as aluminum alloys, mild steel, galvanize steel, copper and magnesium⁸⁻¹⁸. The organic-inorganic hybrid networks are formed by hydrolysis and condensation (sol-gel) reaction of inorganic component (-Si-OR groups) attached to organic moiety. Further, the nature of organic component, presence of reactive functional groups etc. makes it possible to obtain a wide variety of hybrid films²⁵⁻²⁷. These hybrid sol-gel-derived materials are very versatile, combining the complementary properties of the constituting inorganic and organic materials¹⁹⁻²². The organic component controls their hydrophobic nature, elasticity, tenacity, ductility, while the inorganic component provides hardness, stiffness and thermal stability of these hybrid films²³⁻²⁴.

Hybrid coatings based on bis-silane precursors, containing two sets of trialkoxy silane groups on either side of organic moiety as shown Figure 1 below, have been shown to be superior in corrosion resistance performance compared to their mono-functional counterparts²⁸⁻³¹.

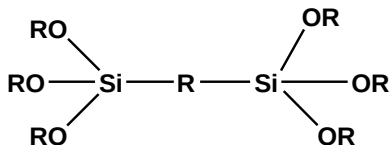


Figure 1: General structure of a bis-silane precursor

Van Ooij et al, have extensively studied different bis-silanes precursors and demonstrated their organic-inorganic hybrid films to be much superior in corrosion resistance in comparison to mono-silanes on Al and Al alloys, steel,

galvanized steel and Mg alloys²⁹⁻³⁰. Their study also concluded that bis-silanes tend to bond metal substrates more strongly than corresponding mono-silanes due to the higher number of Si-OR groups in the former, resulting in a much denser interfacial region through hydrolysis and condensation reactions³¹.

In the present work, a bis-silane precursor has been synthesized by reaction of diglycidyl ether of bis-phenol-A (DGEBA) and 3-(aminopropyl) triethoxysilane (APTES). Using this bis-silane precursor in conjunction with varying amount of TEOS, sol-gel derived OIH coatings have been deposited onto Al-2024-T3 test panels. Corrosion resistance performance of these coatings has been studied using salt spray method.

2. Experimental

2.1. Materials

3-Aminopropyl triethoxysilane (APTES) and tetraethyl orthosilicate (TEOS) was supplied by Acros Organics Ltd, liquid epoxy resin, diglycidyl ether of bis-phenol-A (DGEBA) was supplied by Synpol Ltd., Ahmedabad, India. Ethyl alcohol, Acetone, potassium hydroxide (KOH) and glacial acetic acid (GAA) were purchased from Labort Chemicals, India. All reagents and chemicals used were laboratory grade and used as supplied.

2.2. Sample panels and their surface preparation

Industrial aluminium alloy AA-2024-T3 panels were used as substrate for deposition of sol-gel coatings. The chemical composition of this alloy, as determined by optical emission spectroscopy (OES) was found to be: Fe 1.6, Cu 0.4, Pb 0.1, Zn 0.7, Mn 0.2, Ti 0.05 and balance Al, as % by mass. The sample panels, 6" x 4" x xx" were prepared prior to the application of sol-gel pre-treatment as follows. First, panels were polished successively with 150, 400 and 600 grit sand papers, followed by a rinse with acetone and sonicated in acetone for 15 min. Panels were then immersed in alkaline solution containing KOH (x %) for 10 minutes at 50°C. This treatment provided alkaline etching and chemical activation of the substrate. Panels were then rinsed 4 times with tap water and finally with de-ionized water, and placed vertically in a panel stacker.

2.3. Synthesis of epoxy bis-silane precursor

Epoxy bis-silane precursor was synthesized by reaction of epoxy resin with amino silane compound, namely APTES using 1:1 molar ratio. Into a 500 ml 3-neck reaction flask equipped with a mechanical stirrer, thermometer and an inlet for nitrogen gas, calculated amount of ethyl alcohol and epoxy resin were

charged and the mixture was stirred for 20 min until clear solution was obtained. APTES was then slowly added from an addition funnel, under stirring, at room temperature. After complete addition of APTES, the mixture was stirred for additional 3 hr at room temperature and sample was tested for complete consumption of epoxy groups using FT-IR spectroscopy. The final product precursor was obtained as its solution in ethanol and the solid content was adjusted to 40% by mass, and stored in plastic bottles under a desiccator.

2.4. Preparation of hybrid sols and their application

Preparation of epoxy bis-silane sols and their application were carried out as per the following method.

Step-1: Pre-hydrolysis of TEOS

TEOS was added under stirring to a mixture containing ethanol and deionized water, (2:1 by vol.) that was adjusted to pH of ~ 3.0 using GAA (acid catalyst). The pH of the final solution was solution was adjusted to 3.0 - 3.5 with TEOS content of 10% by wt. The mixture was stirred under magnetic stirrer, at room temperature, for 3 to 24 h.

Step-2: Preparation of sol application bath

A sol application bath was prepared by addition of appropriate quantity of precursor compound (epoxy bis-silane) under stirring into the calculated quantity of pre-hydrolyzed TEOS solution (step-1). After addition was complete, the final solid content (TEOS + epoxy bis-silane) was adjusted to 10% by wt. using deionized water and ethanol. The pH of sol application bath was adjusted to 4.5 - 5. The TEOS quantity was varied from 0 to 6% of sol application bath. For all the samples studied, the ratio of water/ethanol and solid content was maintained constant. Compositions of sol application bath for various systems studied are shown in Table I.

Table I: Designation of Coating Formulation on the basis of TEOS (%) and Hydrolysis Time of TEOS

Coating Designation	TEOS (%)	Hydrolysis time for TEOS (hr)	Solid Content of bath solution (wt %)	Water/ ethanol ratio
Bare	-	-	-	-
S(b)	-	-	10	1:2
S _T 1	2	12	10	1:2
S _T 2	4	12	10	1:2
S _T 3	6	12	10	1:2
S _T 4	4	3	10	1:2
S _T 5	4	12	10	1:2
S _T 6	4	24	10	1:2

After preparation of sol application bath, samples were applied after 30 min and within 2.5 h, by dip coating process. Dip coating was carried out at room temperature and samples were dipped vertically. Samples were immersed into the sol application bath, with immersion residence time of 1 min, and with constant withdrawal rate of 2 cm/min. After application, panels were placed vertically in a panel stacker for air drying. The typical dry-film thickness of coating was approximately 2-5 microns.

3. Characterization methods

3.1. FTIR (Fourier transform infrared spectroscopy)

Epoxy bis-silane precursor was characterized for chemical structure using Fourier Transform Infrared spectroscopy (FTIR). The multi-scan FTIR spectra were recorded at room temperature, in mid operating range of $4,000\text{ cm}^{-1}$ to 400 cm^{-1} .

3.2. Neutral salt-spray test (NSS)

The neutral salt-spray test for the coated specimens was carried out as per ASTM B117 method. The coated specimens were subjected to the continuous salt fog in fog chamber containing 5% sodium chloride solution. The test has been carried out for 500 h and their corrosion resistance performance was rated on a 0-10 scale based on the extent of corrosion or visible damage to the films, with 0 being complete failure and 10 being no corrosion or visible damage to samples.

4. Results and discussion

4.1. Structural characterization of coatings

Figs. 1 and 2 shows the FTIR spectra of pure epoxy resin and epoxy bis-silane precursor respectively.

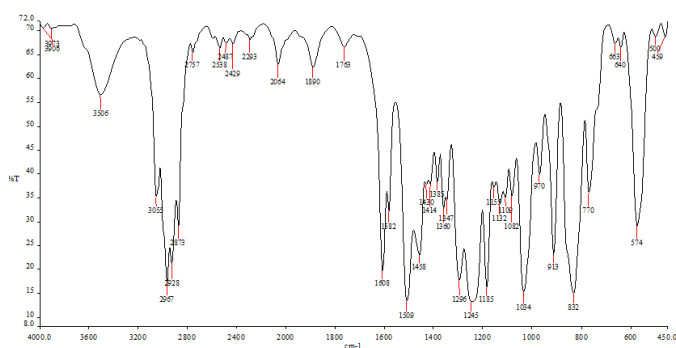


Figure 1: IR spectra of pure epoxy resin

It is evident from the spectra that the peak intensity at 913 cm^{-1} corresponding to epoxide group significantly decreases after the silane modification, which indicates that the epoxide was chemically consumed by silane agent. It is also clear that the peak of -OH at 3435 cm^{-1} appear due to the formation of hydroxyl groups after the open ring reaction of epoxide. It indicates the silane component has been grafted to epoxy resin.

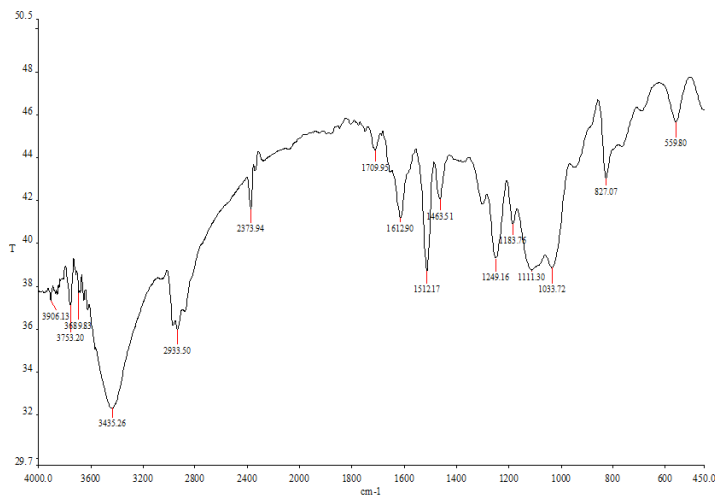


Figure 2: IR spectra of epoxy bis-silane precursor

4.2. Corrosion resistance performance

In order to study the effect addition of pre-hydrolyzed TEOS, we have varied TEOS quantity and hydrolysis time during sol formulation, while keeping all other factor of sol (bath) solution constant (Water/Ethanol/GAA as 1:2:0.050 molar ratios and 10 wt% solid content). A series of coating was prepared with varying TEOS quantity and hydrolysis time 2%, 4%, 6%, 3h, 12h and 24h reported as S_T1 , S_T2 , S_T3 , S_T4 , S_T5 and S_T6 , respectively. After application on aluminum panels were cured at room temperature for two week and tested for corrosion resistance performance by salt spray test.

4.2.1. Neutral salt spray test

Figure 3 shows the images of bare and the sol coated (with and without TEOS) panels after exposure in salt spray chamber. Visible observation shows no blisters, cracking and any corrosion product formation on S_T2 coated aluminium sample after four weeks of exposure. Failure of coating was defined as being three or more pits per panel (according to ISO-10289) or coating delamination. Panels were inspected at 12 h intervals. Upon failure panels were removed. After 24 h significant corrosion product was noted on the bare panel and it was removed from chamber. After 220 h of exposure,

S(b) sol coated panel under goes severe damages. All other panels (Figure 3 S_T1 and S_T3) were removed after completion of 336 h of exposure. Only S_T2 coated panel shows no blisters, cracking and any corrosion product.

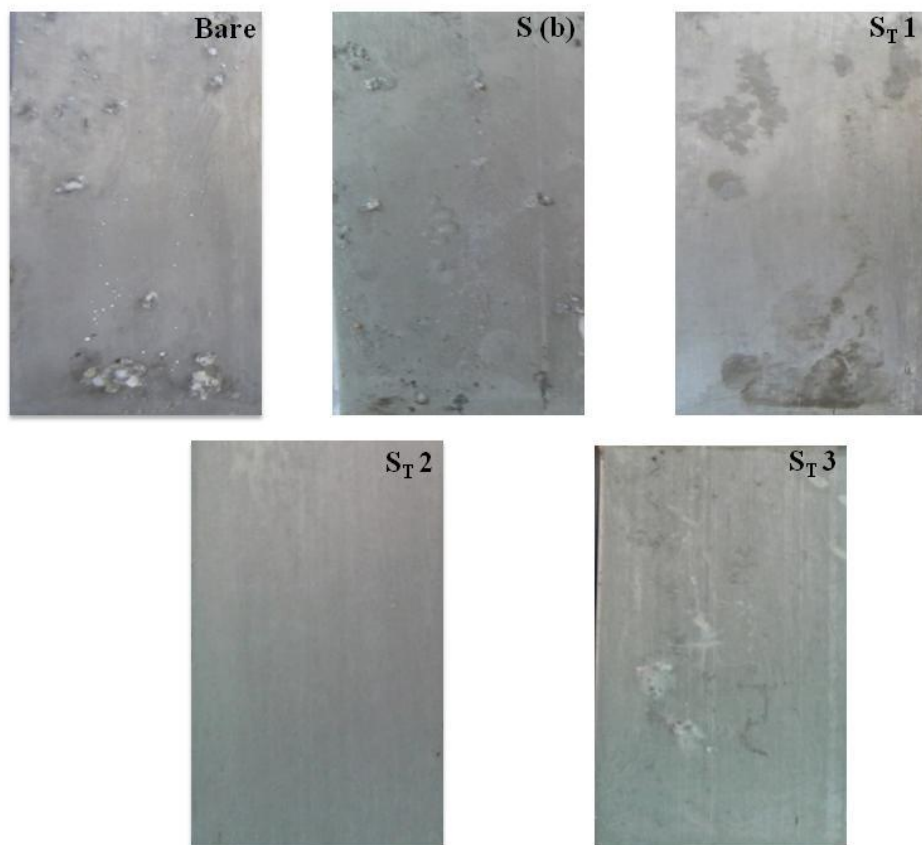


Fig 3: Salt spray images of bare, S(b), ST1, ST2 and ST3 sol coated substrates of aluminium

5. Conclusion

Silane films are excellent surface pre-treatment coatings in that they provide good corrosion protection to AA 2024-T3. The study demonstrates synthesis of organosilanes, epoxy bis-silane precursor, and their usefulness in deriving chromate-free OIH pretreatments on 2024-T3 aluminum alloy, using a modified two-step sol-gel process. The accelerated corrosion test (salt-spray) study clearly shows much lower corrosion rate, indicating the formation of dense coatings, with sol contain 4% TEOS having the best performance. The factors such as quantity TEOS and silane hydrolysis time are the key factors controlling the corrosion performance of the coatings.

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