CHAPTER 1

Water-based sol—gel coatings for military coating applications

Danqing Zhu[1], **Naiping Hu**[2], **Dale W. Schaefer**[2]
[1]Ecosil Technologies LLC, Fairfield, OH, United States; [2]Department of Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, OH, United States

Contents

1. Introduction

A typical military coating system, such as the Chemical Agent Resistant Coating (CARC) system, consists of a metal pretreatment coating, an epoxy primer, and a polyurethane topcoat. These coatings impart excellent corrosion protection to a broad range of metal substrates. However, they also pose health/safety and environmental concerns due to (1) the use of carcinogenic hexavalent chromium compounds as a major pretreatment coating ingredient and as anticorrosion pigments in the epoxy primers and

Handbook of Waterborne Coatings
ISBN 978-0-12-814201-1
https://doi.org/10.1016/B978-0-12-814201-1.00001-9

(2) the high content of organic solvents, often classified as volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), in the epoxy primers. Examples of problematic military coatings are (i) MIL-PRF-23377 (solvent-borne, chromated epoxy primer), (ii) MIL-PRF-85582 (water-reducible, chromated epoxy primer), (iii) DOD-P-15328 (solvent-borne, chromated acid-etching wash primer), and (iv) MIL-DTL-5541 (chromate conversion coating—metal pretreatment).

Driven by strict chromate/VOC/HAP regulations and by demand for improved lifetime of coated military assets exposed in harsh environments, coating formulators have been seeking high-performance coatings that comply with current health and environmental regulations. With its unique merits, sol–gel technology has become especially attractive to the formulators in recent years. The major merits of sol–gel coatings include (1) process flexibility (e.g., ambient spraying or immersion application), (2) highly cross-linked coating structure as an excellent physical barrier to retard the ingress of water/corrosive species, (3) covalent bonding to metals substrates to provide strong adhesion at metal/coating interface, and (4) the use of environmentally friendly sol–gel precursors.

Solvent-based sol–gel coatings have demonstrated excellent corrosion protection performance on metals [1–31]. But the large volume of organic solvents required in the sol–gel process hinders the widespread use of these coatings. Water-based sol–gel coatings have been developed and commercialized. Typical applications of these water-based sol–gel coatings include (1) *passivation coatings* based on organofunctional silanes (1–2 μm) for bare corrosion protection to replace chromate passivation treatment on continuously produced galvanized steel sheets [32,33] and (2) *metal pretreatment coatings* based on zirconium/titanium oxide and/or organofunctional silanes for paint adhesion (20 nm–1 μm) to replace chromate/phosphate-based pretreatments in commercial and military applications [34–38]. In addition, researchers have also demonstrated that anticorrosion performance of waterborne coatings can be enhanced by adding hydrophobic organofunctional silanes [39–43].

This chapter will first introduce the background of sol–gel technology and the chemistry of alkoxysilanes (the most valuable sol–gel precursors) and will then review the evolution of water-based sol–gel coatings for corrosion protection with a focus on their use in military coating applications.

2. Background of sol–gel technology

The sol–gel technology is very attractive for materials synthesis because it allows direct fabrication of multicomponent materials in different configurations (monoliths, coatings, and fibers) without the use of expensive vacuum technologies [44,45]. The most important commercial sol–gel products are films and coatings. Fig. 1.1 illustrates a sol–gel process and a variety of sol–gel derived materials.

2.1 What is a sol–gel process?

The term "sol–gel" is an abbreviation for "solution gelling." As shown in Fig. 1.1, a solution or a "sol" of dissolved precursors in a liquid phase is transformed to the solid state through a sequence of chemical reactions that involve polymerization at ambient temperatures. A "gel" is an interconnected three-dimensional network formed by uniform polymerization of the sol throughout the liquid medium. As gelation proceeds, the rigidity of the product increases. There are two types of well-recognized sol–gel processes:

Type I: formation of a network by destabilization of dispersed colloidal particles in a liquid, resulting in particulate gels;

Type II: hydrolysis and polycondensation reactions of metal alkoxides, resulting in alkoxide gels [46].

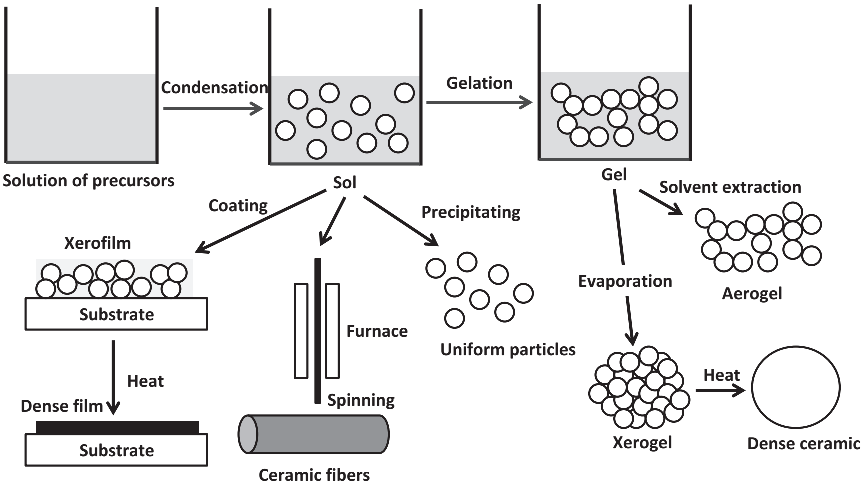


Figure 1.1 Illustration of a sol–gel process and a variety of sol–gel derived materials.

A sol–gel process generally involves the following stages [47]:

- *Hydrolysis* of precursors
- *Condensation and polymerization* to form chains and particles, leading to viscosity increase
- *Gelation* to form a network that entraps the remaining solution. This step includes both hydrolysis and condensation as the percolating network engulfs the entire solution
- *Aging* to form further cross-links, with covalent links replacing nonbonded contacts leading to structural evolution including changes in pore size and pore wall strength
- *Drying* for the loss of water, alcohol, and other volatile components

Type II is the most widely used sol–gel process, which starts with a solution of monomeric metal alkoxide precursors $M(OR)_n$ in an alcohol or other low molecular weight organic solvent. Here M represents metal elements, such as Si, Ti, Zr, Al, Fe, B, etc, and R is typically an alkyl group (C_xH_{2x+1}) [48]. Application methods include dip coating, spin coating, spraying, and electrodeposition [49–52].

Compared to other metalloid alkoxides, alkoxysilanes (metalloid alkoxides of Si) react toward water in a less aggressive or more controllable way [53,54]. This makes alkoxysilanes the most valuable sol–gel precursors in preparation of sol–gel materials and coatings. The chemistry of alkoxysilanes is discussed in the following sections.

2.2 Chemistry of alkoxysilanes

2.2.1 Silane coupling agents

Silanes refer to monomeric silicon compounds. A silane that contains at least one silicon–carbon bond ($Si{-}CH_3$) is an organosilane. Organofunctional silanes are molecules carrying two different types of reactive groups attached to the silicon atom so that they can react and couple to an inorganic surface (e.g., ceramics and oxide layers on metals) or to organic resins via covalent bonds [55]. Organofunctional trialkoxysilanes were first demonstrated in 1940 to be effective adhesion promoters or coupling agents during the development of fiberglass-reinforced composite [56,57]. A general molecular structure of organofunctional trialkoxysilanes is as follows:

$$R'(CH_2)_nSi(OR)_3, \text{ where } n = 0, 1, 2, 3 \ldots.$$

Two types of reactive groups in the above silane molecule are (1) an organofunctional group or organic group (R′) such as epoxy, amino, methacryloxy, or sulfide and (2) hydrolyzable or leaving alkoxy group (OR) such as methoxy (OCH_3), ethoxy (OC_2H_5), and acetoxy ($OCOCH_3$).

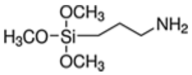
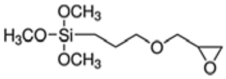
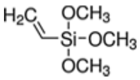
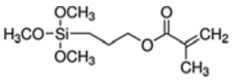
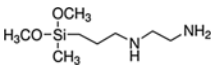
Researchers found that certain organofunctional trialkoxysilanes significantly improved the composite mechanical strength by preventing ingress of water and bond displacements at the fiber/resin interface [57]. Nowadays, the widespread use of organofunctional silanes can be found in coatings/paints, adhesives, and sealants. Table 1.1 lists some representative silane coupling agents.

2.2.2 Key reactions of silane coupling agents

Molecules of organofunctional trialkoxysilanes undergo two key reactions, *hydrolysis* and *condensation*, during applications.

- *Hydrolysis* to convert hydrolyzable groups (OR) to silanols (Si—OH) in the presence of water or moisture in the atmosphere
- *Condensation* among silanols (Si—OH) to form a three-dimensional siloxane (Si—O—Si) structure
- *Condensation* with hydroxyl groups on an inorganic substrate to form covalent bonds

Table 1.1 Representative silane-coupling agents.

Name	Molecular structure	Organofunctional group
(3-Aminopropyl)trimethoxysilane		Primary amine
(3-Glycidyloxypropyl)-trimethoxysilane		Epoxy
Vinyltrimethoxysilane		Vinyl
3-(Trimethoxysilyl)propyl methacrylate		Methacrylate
3-(2-Aminoethylamino)-propyldimethoxymethylsilane		Diamine

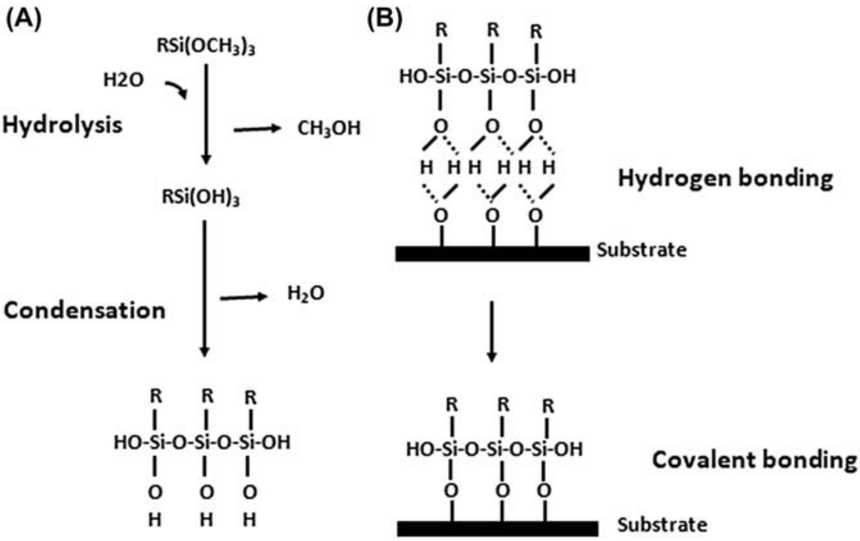


Figure 1.2 The process for organofunctional trialkoxysilane hydrolysis, condensation, and covalent bonding to an inorganic substrate; (A) hydrolysis and condensation to form oligmers in the silane solution and (B) adsorption to an inorganic substrate (such as ceramics or surface oxide layers on metals) by hydrogen bonding and then covalent bonding to the substrate by a condensation reaction with hydroxyl groups [55].

Fig. 1.2 schematically shows the process for organofunctional trialkoxysilane hydrolysis, condensation, and covalent bonding to an inorganic substrate [55].

Silane hydrolysis and condensation reactions, as shown in Fig. 1.2A, can be catalyzed by either an acid or a base. Mechanisms of acid- and base-catalyzed hydrolysis and condensation have been studied [56,58]. Important findings are as follows: (1) the rate of hydrolysis by both mechanisms is influenced by the nature of the organic group and the leaving alkoxy group attached to the silicon atom, and (2) pH also affects the hydrolysis rate, and the optimum pH for hydrolysis is not optimum for condensation. Therefore, determining the best balance between hydrolysis and condensation is one of the keys to the successful utilization of organosilane chemistry for special application.

Silane covalent bonding to an inorganic substrate, as shown in Fig. 1.2B, takes place via the following two steps. In the first step, silanol (Si—OH) groups from the hydrolyzed silanes adsorb to the inorganic substrate via hydrogen bonding to surface hydroxyl groups such as silanol (Si—OH) groups on a glass surface or Al hydroxyl (Al—OH) groups on an aluminum surface. In the second step, the adsorbed silanol groups condense with surface hydroxyl groups to form siloxane (Si—O—Si) covalent bonds on glass or metallosiloxane (Me—O—Si) covalent bonds on a metal surface, releasing water [56].

It is generally accepted that siloxane bonds formed at the silane/glass interface are hydrolyzable during long-term exposure to water and are reformable when dried [56]. No direct evidence has been available so far for the equilibrium conditions at the interface, but the reversible nature of the siloxane-bonded interface has been demonstrated in performance testing. Bonding of a trialkoxysilane $R'Si(OH)_3$ to silica has a much greater improvement in water resistance than a simple alkoxy bond between a hydroxyl functional polymer and silica. This improvement is because trialkoxysilane presents a more hydrophobic and highly cross-linked interphase region.

Silane bonding to polymers has also been studied [57,58]. Good adhesion of silanes to polymers is attributed to two mechanisms: (1) chemical reactions occurring between organofunctional groups in the silanes and reactive groups in the polymers and (2) the formation of interpenetrating networks (IPNs) at the silane/polymer interface.

In brief, silane coupling agents perform as a "bridge" to promote adhesion between inorganic substrates (such as glass or oxide layers on metals) and polymers. Silanes react with inorganic surfaces to form metallosiloxane covalent bonds for strong adhesion between silanes and inorganic substrates, while they react with polymers to form chemical bonds and IPNs for good silane/polymer adhesion.

2.2.3 Other organofunctional trialkoxysilanes used in the corrosion control of metals

In addition to silane coupling agents, bis-trialkoxysilanes ("bis-silanes" hereon) have also drawn the attention of coating formulators. Bis-silanes are a special group of trialoxysilanes, that have been used as cross-linkers for silane coupling agents [56]. Due to their unique molecular structure, bis-silanes produce a much denser coating structure than traditional silane coupling agents. Vanooij and coworkers first evaluated bis-silane—based surface treatment coatings for replacing chromate conversion coatings [21–26,59–63] and bis-silane—modified waterborne coatings for replacing chromated epoxy primers in military applications [39–43]. The molecular structure of bis-silanes is as follows:

$$(RO)_3Si(CH_2)_nR'(CH_2)_nSi(OR)_{3,}\ \text{where } n = 0,\ 1,\ 2,\ 3\ \ldots.$$

A major difference between bis-silanes and silane coupling agents listed in Table 1.1 is that silane coupling agents have one Si atom per molecule, attached by three hydrolyzable groups (OR), while bis-silanes have two Si atoms per molecule linked to six OR groups. Assuming all OR groups hydrolyze for both silanes, the former would generate a maximum three silanol (SiOH) groups per molecule while the bis-silanes yield six SiOH groups per molecule. After condensation of SiOH groups, a cross-linked bis-silane film is expected to be denser than a cross-linked film prepared from a silane coupling agent. Examples of bis-silanes are bis-[triethoxysilyl] ethane, bis-[triethoxysilylpropyl]tetrasulfane (bis-sulfur silane), and bis-[trimethoxysilylpropyl]-amine (bis-amino silane). In addition to bis-silanes, tetra-alkoxy silane ($Si(OR)_4$, TEOS), having one Si atom attached by four hydrolyzable OR groups, is another commonly used sol–gel precursor for making a hydrophobic coating on metals for corrosion protection.

3. Water-based sol–gel coatings in military applications

3.1 Early research for sol–gel coatings on metals for corrosion protection in military applications

Early research focused on evaluating solvent-based sol–gel coatings derived from metal alkoxides such as TEOS and zirconium propoxide for metal protection [1–10]. These sol–gel coatings can effectively protect metals from corrosion, but they have major drawbacks that hinder practical application. These drawbacks include the following: (1) oxide films are brittle and thick (>1 μm) and tend to crack, (2) relatively high temperature is required for curing (ranging from 500 to 850°C), and (3) in most cases, organic solvents are needed during the formation of sol–gel coatings [30]. Subsequent researchers found that the addition of organic components can mitigate the brittleness of these sol–gel coatings to a certain extent. Examples are polymethylmethacrylate (PMMA)-ZrO_2 coating and SiO_2-PVB (polyvinyl butyral) coating [4,23]. The use of organofunctional silanes as a major precursor for preparing sol–gel coatings is another effective way to mitigate brittleness and avoid high-temperature curing [30].

Air Force Research Laboratory has investigated sol–gel coatings on aerospace aluminum substrates for corrosion protection [13–20,24,25]. Voevodin et al. formulated hybrid sol–gel coatings from ZrO_2–TEOS–GPS [13] and SiO_2-vinylpolymer systems [14]. A two-stage pitting corrosion mechanism was observed for sol–gel coated Al 2024-T3.

This finding suggests that the corrosion resistance of the sol—gel coatings can be improved by eliminating cracks in the coating and by the addition of inhibitors to prevent pit initiation.

Voevodin et al. [19,20] developed sol—gel coatings based on the self-assembled nanophase particle (SNAP) approach in order to replace the traditional chromate conversion coating on aircraft aluminum alloys. Electrochemical analysis indicated that the 1-μm thick SNAP coating obtained from an aqueous sol—gel process has excellent barrier property and thus has good potential for long-term corrosion protection.

Zhu et al. [21,22] prepared a sol—gel coating on Al 2024-T3 using bis-[3-(triethoxysilyl)propyl]tetrasulfide (bis-sulfur silane) to replace chromate conversion coatings. The bis-sulfur silane coating is very hydrophobic, serving as an excellent physical barrier to postpone the ingress of water/corrosive species (e.g., chloride ions). The hydrophobicity of the coating is attributed to two factors: (1) the hydrophobic sulfide group ($-S_4-$) retained in the bis-sulfur silane coating and (2) a highly cross-linked, three-dimensional siloxane (Si—O—Si) network. The addition of a small amount of silica nanoparticles (e.g., 15 ppm) in the bis-sulfur silane coating leads to a thicker and harder coating that also shows better protective ability in a 3.5% NaCl solution [22].

The bis-silane coating structure on Al 2024-T3 was further characterized using electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM)/energy-dispersive spectroscopy [22,63]. The work revealed that there are three distinct regions formed on a silane-coated metal surface. Fig. 1.3 shows a schematic structure of a silane-coated Al surface. From outside to inside, (1) an outermost cross-linked silane film dominated by Si—O—Si bonds for improved water resistance, (2) an interfacial layer enriched with both Si—O—Si and Al—O—Si bonds, and (3) an innermost aluminum oxide layer.

Results from in these earlier studies indicated that sol—gel coatings provide excellent corrosion protection for metals. However, the use of organic solvents during the sol—gel process is not desired. Recent developmental efforts have successfully yielded several water-based sol—gel coatings compatible with a variety of applications. The following two groups of sol—gel coatings have been evaluated in military applications: (1) water-based sol—gel pretreatment coatings as a replacement for chromate and phosphate pretreatments and (2) waterborne coatings enhanced by bis-silanes (“super primer”) as a replacement for chromated epoxy primers.

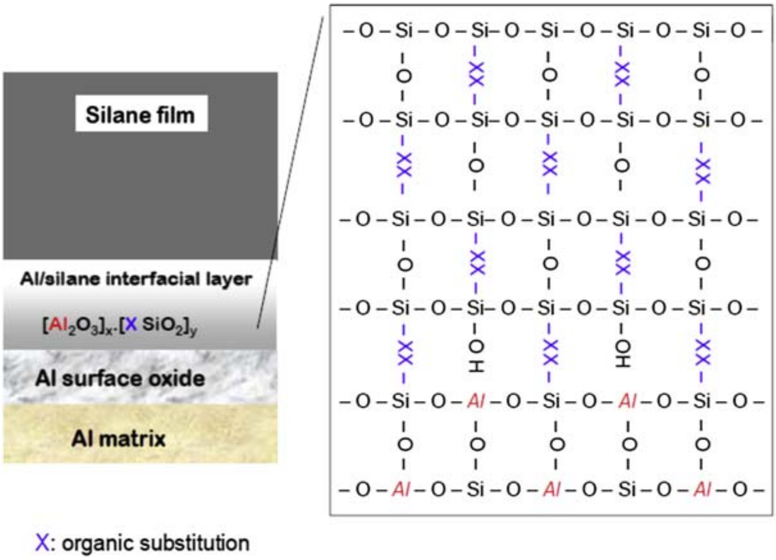


Figure 1.3 A schematic structure of silane-coated Al surface [63].

3.2 Water-based sol—gel pretreatment coatings

Hexavalent chromium (Cr(VI)) conversion coatings and phosphate-based pretreatments have been used for decades in coating industries, providing excellent paint adhesion and anticorrosive performance over a broad range of metal substrates. However, the use of these pretreatments is highly regulated due to the toxic chemicals involved [64—66]. As a response, alternative pretreatment coatings based on different chemistries have been developed. Zirconium oxide—based pretreatment coatings and organofunctional silane-based pretreatment coatings are derived from the sol—gel technology [32—38]. These coatings form rapidly on metal surfaces by ambient spraying or immersion/dipping, with a typical coating thickness ranging from 20 nm to 1 μm.

3.2.1 Water-based organofunctional silane—based pretreatment coatings

Organofunctional silanes that contain hydrophilic organic groups such as amino groups can hydrolyze readily without the need of an organic solvent. Zhu [63] prepared an aqueous silane solution using bis-[trimethoxysilylpropyl]amine (bis-amino silane) and vinyltriacetoxy-silane. Marine alloy panels (AL-6XN, a type of weldable stainless steel consisting of nickel [24%], chromium [22%], and molybdenum [6.3%]) were alkaline-cleaned and surface-treated with the solution. The silane-treated panels were then painted with a rosin-based copper (Cu)-antifouling paint. The painted panels were immersed in fresh, filtered (5—10 μm) natural seawater (Wrightsville, NC) for 9 months in a crevice corrosion test. The control panel in this test was cleaned-only without any pretreatment and was coated with an epoxy primer. Fig. 1.4 shows the panels after the first 3-month immersion. The control panel (Fig. 1.4A) exhibits crevice corrosion formed at the metal/epoxy interface, while no sign of crevice corrosion is seen for the silane-pretreated and Cu-antifouling painted panel (Fig. 1.4C). No crevice corrosion was seen after 9 months of immersion.

OXSILAN AL-0500 (Chemetall GmbH), a silane-based multipurpose pretreatment product for aluminum substrates, has been examined as a replacement for chromate conversion coatings on aluminum alloys 2024, 2219, 5083, and 7075 under military coatings in accelerated corrosion tests [67]. The test panels were pretreated with OXSILAN AL-0500 solution to form a thin coating (16 mg/ft^2). These pretreated panels were then coated with military epoxy primers such as MIL-DTL-53022 (a solvent-born, lead- and chromate-free corrosion-inhibiting epoxy primer) and MIL-DTL-53030 (a water-reducible, lead- and chromate-free corrosion-inhibiting epoxy primer) and topcoats such as MIL-PRF-85285 (a high-solid, aliphatic polyurethane coating). The coated aluminum alloy panels were subject to performance tests listed in Table 1.2 [67]. The test results

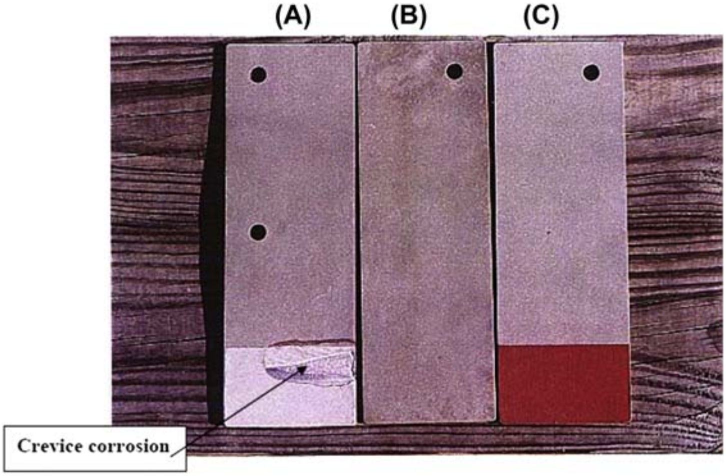


Figure 1.4 Representative view of 3-month ocean-immersed AL-6XN panels; (A) epoxy-coated only, (B) silane-treated only, and (C) silane-treated, followed by Cu-antifouling painted.

Table 1.2 Engineering and testing requirements [67].

Engineering requirements	Tests	Acceptance criteria
Corrosion resistance	Neutral salt fog on unpainted substrate with pretreatment	• Class E: 7 days with no visible sign of corrosion whatsoever; spots and discoloration are acceptable; lightning of coating is acceptable. • Class B1: 7 days with no visible sign of corrosion; lightning of coating is acceptable. • Class B2: 14 days with no visible sign of corrosion, lightning of coating is acceptable.
Corrosion resistance	Neutral salt fog on scribed, painted substrate	• Class C: 3000 h with no evidence of corrosion (minor surface corrosion in scribe permissible).
Corrosion resistance	SO_2 salt fog on scribed, painted substrates	• Class C: 500 h with no evidence of corrosion (minor surface corrosion in scribe permissible).
Corrosion resistance	Cyclic corrosion test on scribed, painted substrates	• Class C: Equivalent or improved performance compared to controls.
Corrosion resistance	Filiform corrosion resistance	All filaments $\leq 1/4''$; majority $<1/8''$.
Corrosion resistance	Marine atmospheric test (beach test) exposure on scribed, painted substrates	• Class C: Equivalent or improved performance compared to chrome controls.
Adhesion	Wet tape adhesion and water resistance of printed substrates	Method A: Rating of $\leq$4A.
Adhesion	Dry tape adhesion of painted substrates	Method B: Loss of two or more complete primer squares shall constitute failure ($\leq$4B).
Electrical resistance	Electrical conductivity of unpainted, pretreated substrates	• <5 milliohms/square inch as coated.

Table 1.2 Engineering and testing requirements [67].—cont'd

Engineering requirements	Tests	Acceptance criteria
		• <10 milliohms/square inch after 168 h neutral salt fog exposure.
Environmental, Safety, and Occupational Health (ESOH)	Toxicology	Less toxic than MIL-C-81706 chromate conversion coating control per EPA toxicity categories (40 CFR 156.10).
Reparability	Reparability	Corrosion resistance, paint adhesion, and electrical contact resistance equal to or better than controls.

show acceptable performance in some cases, yet this pretreatment is not sufficiently universal to replace chromate conversion coatings on aluminum alloys.

3.2.2 *Water-based zirconium oxide pretreatment coatings*

Gusmano et al. [68] deposited zirconium oxide (ZrO_2) coatings by the sol–gel process on aluminum 1050 sheets using two different precursors: (1) a 0.1 M solution of zirconium tetrabutoxide ($Zr(OBun)_4$), containing acetic acid as a complexing agent and (2) a 0.4M solution of zirconyl nitrate ($ZrO(NO_3)$). Coating characterization was carried out using atomic force microscope, X-ray photoelectron spectroscopy (XPS), and electrochemical noise analysis. The ZrO_2 coatings were found to be amorphous, continuous, about 18–30 nm thick, and to provide corrosion resistance comparable to chromate coatings. In addition, hexafluorozirconic acid (H_2ZrF_6) and zirconium salts with hydrofluoric acids (HF) have also been commonly used to form zirconium oxide pretreatment coatings for metals [69–71]. Verdier et al. [72,73] studied ZrO_2 coatings formed by modified aqueous baths of H_2ZrF_6 and hexafluorotitanic acid (H_2TiF_6) on a Mg–6%Al alloy, AM60, using XPS, SEM, and cyclic voltammetry. Film formation occurred by precipitation of zirconium or titanium complexes onto metal surfaces. Precipitation is initiated by an increase in interfacial pH resulting from cathodic water reduction reaction. Examples of commercial water-based zirconium oxide pretreatment coatings are Bonderite TecTalis (Henkel Corp.)

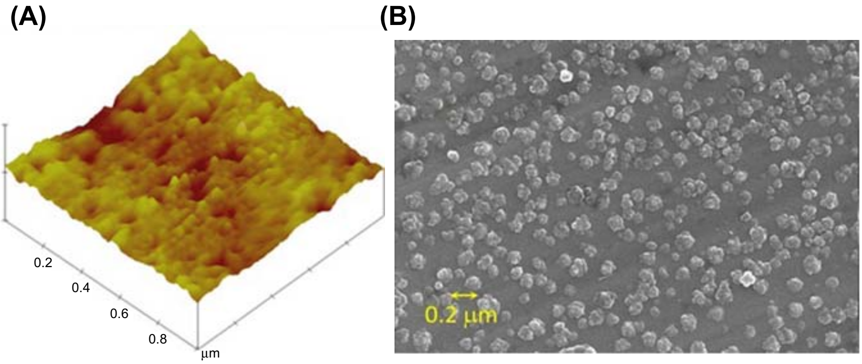


Figure 1.5 Surface morphological images of zirconium oxide pretreatment coatings formed on CRS; (A) 3D topography image of polished CRS sample treated in TecTalis without large clusters (image size: 1 µm× 1 µm, Z-range: 50 nm) (Henkel Corp) [74] and (B) SEM image of Zircobond coating (PPG Industries.) [75].

and Zircobond (PPG Industries). Fig. 1.5 displays the surface morphologies of these zirconium oxide pretreatment coatings on cold-rolled steel (CRS) [74,75].

Ref. [75] also added $ZrO(NO_3)_2$, as a second zirconium source, into a zirconium oxide pretreatment coating (a Zircobond coating) for further performance enhancement. The X-ray fluorescence results indicated that the addition of $ZrO(NO_3)_2$ yielded an increase of deposited zirconium (presumably oxide) film. Fig. 1.6 compares the SEM images of zirconium oxide pretreatment coatings with and without $ZrO(NO_3)_2$ modification. These two pretreatment coatings were immersion-applied onto CRS and were then coated with an MIL-DTL-53022 epoxy primer. The coated CRS panels were subject to accelerated corrosion tests in accordance with GMW 14872 and ASTM B117. The results, however, did not show significant performance improvement for the $ZrO(NO_3)_2$-modified pretreatment coating.

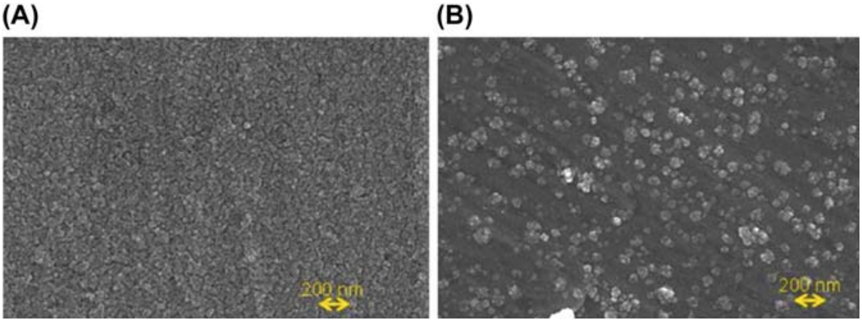


Figure 1.6 SEM images of zirconium oxide coatings modified with (A) and without (B) $ZrO(NO_3)_2$ [75].

3.2.3 Water-based hybrid pretreatment coatings

Both silane-based and zirconium oxide pretreatment coatings are currently being used commercially in automotive and general industries for enhanced paint adhesion and corrosion protection. However, some inherent drawbacks have been noticed for these pretreatments during industrial production settings.

Flash rusting of carbon steel associated with zirconium oxide pretreatment coatings: As a major type of engineering materials, carbon steel has been widely used in many applications. However, carbon steel is prone to rapid corrosion, known as "flash rusting," that instantly occurs when the metal is exposed to humid or aqueous corrosive environments. This powdery flash rust formed on the steel surface drastically weakens subsequent paint adhesion. A carbon steel surface treated with an acidic zirconium pretreatment solution is more susceptible to "flash rusting" if the treated steel surface is not sufficiently rinsed by deionized (DI) water to remove acidic components and free fluoride ions (F^-) from the surface. In some cases, especially during production line stoppages, flash rusting still readily occurs on zirconium oxide-treated carbon steel surface after post DI water rinse. Because of this limitation, the zirconium oxide pretreatment coating is not suggested for use in "dry-in-place" processes where no DI water postrinse step is applied.

Limited paint compatibility of silane-based pretreatment coatings on paint types: Organofunctional silane-based pretreatment solutions are less corrosive than zirconium pretreatment solutions. A cross-linked silane pretreatment coating mitigates flash rusting of carbon steel to a certain extent. However, the major drawback of silane-based pretreatment coatings is that they are "picky" regarding the subsequently applied paint type. Therefore, matching of organofunctional groups on the silane molecule(s) to the polymer (paint) type is a must to ensure excellent paint adhesion. However, this stipulation may not be practical in industrial settings.

Hybrid pretreatment coatings have thus emerged as a solution to overcome the inherent drawbacks of the above pretreatment coatings. The hybrid pretreatment coatings are formed by combining two different types of sol–gel precursors that often contain organic and inorganic components. Examples of hybrid pretreatment coatings are Boegel (Boeing Company) [76–78] and SILSBOND (Ecosil Technologies) [79].

Boegel refers to a family of water-based sol–gel coatings that can be applied to a range of substrates such as aluminum, titanium, nickel, and steel using a variety of methods. A key application for Boegel-EPII, one Boegel formula, is as a nonchrome surface treatment for the exterior of commercial aircraft. Generic components of Boegel-EPII are 1 wt% zirconium n-propoxide and 2 wt% 3-glycidoxypropyltrimethoxy silane in DI water with glacial acetic acid as a catalyst [78].

It is hypothesized that the difference in condensation rates between the silane and zirconium components produces a hybrid inorganic/organic layer with a compositional gradient from the metallic surface to the subsequent coating layer [78]. XPS results for a Boegel-EPII coating on clad Al 2024-T3 revealed that Si from silane is found predominantly at the surface of the coating, while the amount of Zr increases with sputtering time, suggesting the aluminum substrate and the Boegel coating relies primarily on Zr—O—Al covalent bonding. The thickness of the sol—gel coating can be controlled by varying the formation chemistry, with a range of 20 nm—1 μm.

The combination of inorganic and organic components in the Boegel coatings yields unique properties. For example, the thin sol—gel coatings are more flexible than an inorganic metal oxide film of similar thickness as demonstrated by comparing the flexibility of aluminum alloy panels treated with either the Boegel-EPII coating or a chromic acid conversion coating (CCC). When subjected to a conical mandrel bending test at low temperatures (−54°C), the CCC-treated Al surface cracked, whereas the Boegel-EPII—treated surface showed no cracks [78].

The performance of the Beogel coating on the B777-200LR was assessed after 9 months of flight testing. The adhesion of the coating system was excellent with no exposed rivets. Depending on the size of the aircraft, between 100 and 400 gal of chromated coatings and rinse water per plane are eliminated by replacing the CCC coating [78].

Boegel-EPII coating has also been examined as a replacement for chromate conversion coatings for aluminum alloys 2024, 2219, 5083, and 7075 under military primers such as MIL-PRF-53022 and MIL-53030 and topcoats such as MIL-PRF-85285, along with OXSILAN AL-0500 [67]. The coating weight of Boegel-EPII coating on Al 2024 was 22.40 mg/ft^2.

SILSBOND hybrid pretreatment coatings have a generic formula consisting of aqueous silsesquioxane oligomers and transitional metallic acid such as H_2ZrF_6. A typical 20—50 nm thick SILSBOND coating forms on a metal surface by immersion or by spraying without post-DI water rinse. Fig. 1.7 compares the surface morphologies of CRS deposited with and without a SILSBOND pretreatment coating. The CRS surface treated with SILSBOND solution exhibits a uniform distribution of nanoparticles (presumably ZrO_2). The particle size ranges from a few nanometers to 25 nm.

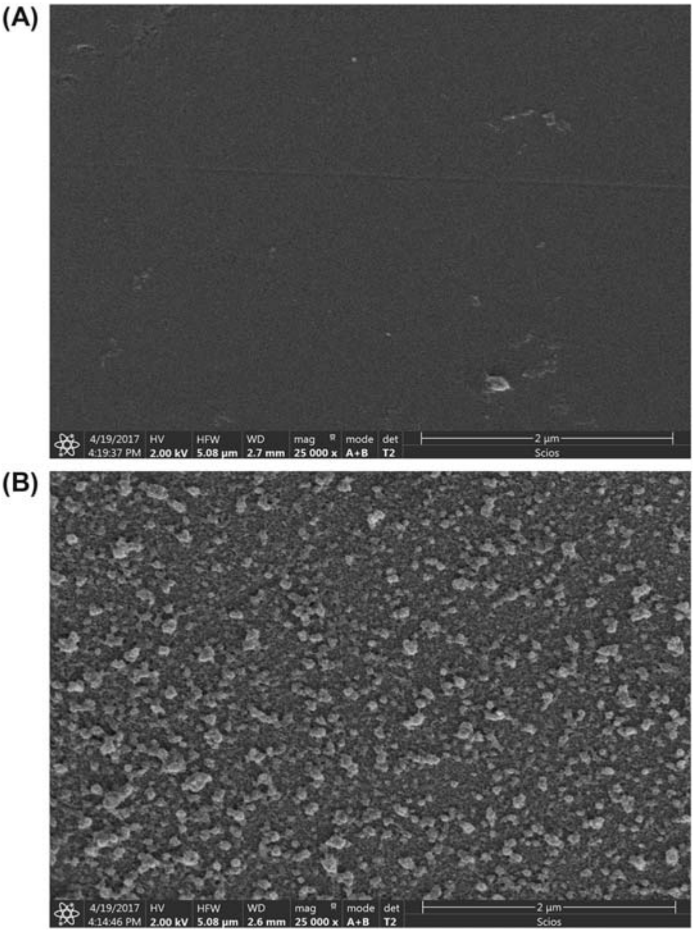


Figure 1.7 SEM images of CRS surfaces; (A) polished surface, (B) deposited with a SILSBOND pretreatment coating (the scale bar in the figure is 2 μm).

SILSBOND coating structure on aluminum surface was further characterized by X-ray reflectivity (XRR). In this study, a 100 nm Al layer was first vapor-deposited onto a smooth Si wafer surface, and then the Al-coated Si wafer surface was immersed in a SILSBOND pretreatment solution for 30 s. Fig. 1.8 shows the XRR plots for the Al-coated Si wafer surface before and after being treated with a SILSBOND solution. As seen in Fig. 1.8, the reflectivity curve for the Al-coated Si wafer surface before SILSBOND treatment ($t = 0$ s) shows two types of fringes: (1) closely spaced fringes in the q range from 0.5 to 0.7 nm^{-1} representing the 100 nm

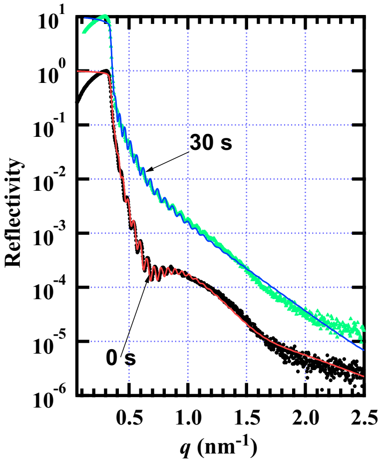


Figure 1.8 XRR plots for Al-coated Si wafer surface before and after being treated with a SILSBOND solution.

Al layer on Si wafer and (2) the hump in the q range from 0.7 to 1.5 nm^{-1} due to the aluminum oxide layer naturally formed on the surface. After 30 s of immersion in the SILSBOND solution, the hump for the Al oxide layer completely disappears, implying that the Al oxide layer has been completely stripped during immersion in the SILSBOND solution. This effect is likely due to the attack of F^{-} ions (from H_2ZrF_6) on the Al oxide and the Al substrate.

The XRR data in Fig. 1.8 were further interpreted by fitting the reflectivity versus q profiles with a four-layer model [80]. Fig. 1.9 shows the resulting scattering length density (SLD) profiles. In Fig. 1.9, the surface Al oxide layer on the treated Al-coated Si wafer is revealed by the rounded SLD profile ($t = 0$ s). After 30 s of immersion in the SILSBOND solution, the Al oxide layer is replaced by a 5 nm-thick Zr-rich layer that is indicated as a spike in the SLD profile. Also, a ~20 nm-thick layer of lower SLD is observed next to the Zr-rich layer. The lower SLD values indicate this layer is organic-rich. Taking account of the surface morphological image of SILSBOND shown in Fig. 1.7, the SILSBOND coating has two distinct regions:

(1) A 5 nm-thick Zr-rich inner layer, which is likely a region consisting of numerous ZrO_2 nanoparticles tightly anchoring to the metal surface

(2) A 20 nm-thick organic-rich outer layer, which is likely a mixed region consisting of a highly cross-linked silsesquioxane network embedded with ZrO_2 nanoparticles.

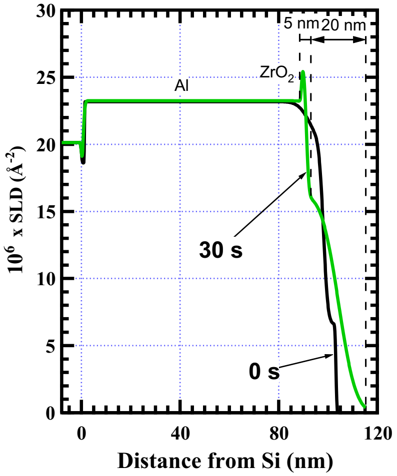


Figure 1.9 Fitted SLD profiles for Al-coated Si wafer surface before and after being treated with a SILSBOND solution.

Its unique coating structure may explain why SILSBOND not only provides enhanced paint adhesion but also mitigates flash rusting of carbon steel. Paint adhesion enhancement may be attributed to two factors: (1) F^- ions attacking to remove metal surface oxides and contaminants resulting in a clean, good-wetting metal surface and (2) deposition of numerous ZrO_2 nanoparticles creating a roughened metal surface that provides a mechanical interlocking effect for enhanced paint adhesion. Mitigation of flash rusting is likely due to the sealing effect of the continuous organic-rich outer layer. This layer covers the bare steel surfaces between ZrO_2 nanoparticles to prevent the exposure of these areas to moisture. Additionally, organo-functional groups retained in the outer layer also contribute to paint adhesion by chemically reacting with paints and by forming IPN with the paint.

SILSBOND pretreatment coatings have recently been evaluated as a replacement of DOD-P-15328D (solvent-borne, chromated wash primer) in military applications [81,82]. DOD-P-15328D wash primer has been used extensively as one workhorse pretreatment portion of the CARC coating system for steel and aluminum substrates, especially in coating repair applications.

In this work [81], the SILSBOND pretreatment solution was sprayed onto metal substrates including Al 6061, CRS, HDG, and stainless steel. These panels were then painted with CARC coatings. These painted metal panels were subject to adhesion test (ASTM D3359), pencil hardness test

(ASTM D3363), cyclic corrosion test (GM 9540P), outdoor weathering test, and salt spray test (ASTM B117). Figs. 1.10—1.11 show the performance of SILSBOND pretreatment coatings on CRS panels under MIL-DTL-53022 epoxy primer in accelerated corrosion tests in accordance with GM 9540P and ASTM B117. The control system was DOD-P-15328D wash primer. The results indicated that SILSBOND pretreatment

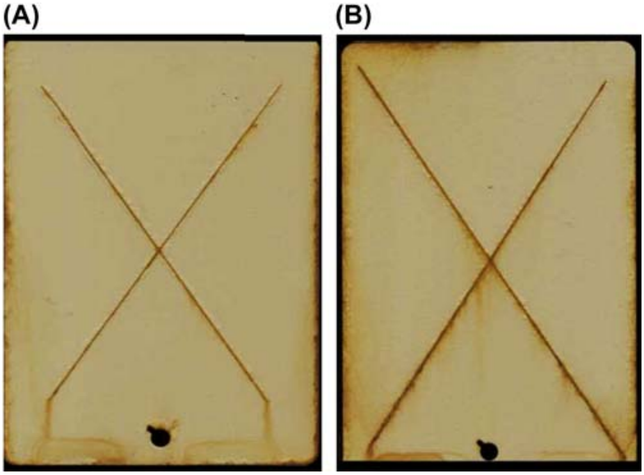


Figure 1.10 MIL-PRF-53022 epoxy primer—coated CRS panels after 80 cycles of GM 9540P (A) Eco 5-1 (a SILSBOND coating) pretreated; (B) DOD-P-15328D pretreated [81].

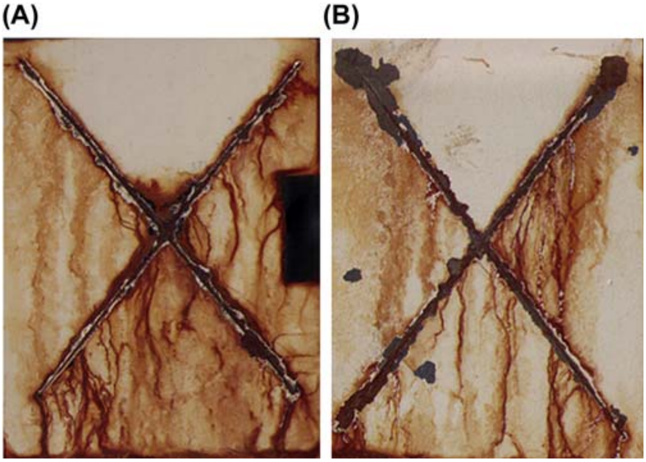


Figure 1.11 Abrasive-blasted CRS panels coated with MIL-P-53022D after 1000 h of ASTM B117; (A) SILSBOND pretreated, (B) DOD-P-15328D pretreated [81].

offers equivalent anticorrosion performance as DOD-P-15328D wash primer.

3.3 Waterborne coatings enhanced by organofunctional trialkoxysilanes

Vanooij and coworkers added hydrophobic bis-silanes into waterborne coatings for enhanced corrosion protection [39–43]. The objective of this work was to develop a two-in-one type primer (also named "super primer") to replace both chromate conversion coating and chromated epoxy primers in military coating systems. The super primers have a generic formula consisting of (1) water-based resins and their cross-linkers, (2) bis-silanes (hydrolyzed or nonhydrolyzed), and (3) nonchromate anticorrosive pigments. Fig. 1.12 illustrates the preparation of super primer.

Fig. 1.13 compares the Al 2024-T3 panels coated with a super primer (water-based epoxy acrylic resin mixed with 10% nonhydrolyzed bis-sulfur silane) and with solvent-borne chromate-containing epoxy primer (MIL-PRF-23377J) after 2 months of immersion in a 3.5% NaCl solution. The panel coated with chromate-containing epoxy primer (Fig. 1.13A) shows blisters on the scribe line, while no blisters and paint loss were observed for the super primer–coated Al panel (Fig. 1.13B). This result indicated that the super primer has the potential to replace the traditional

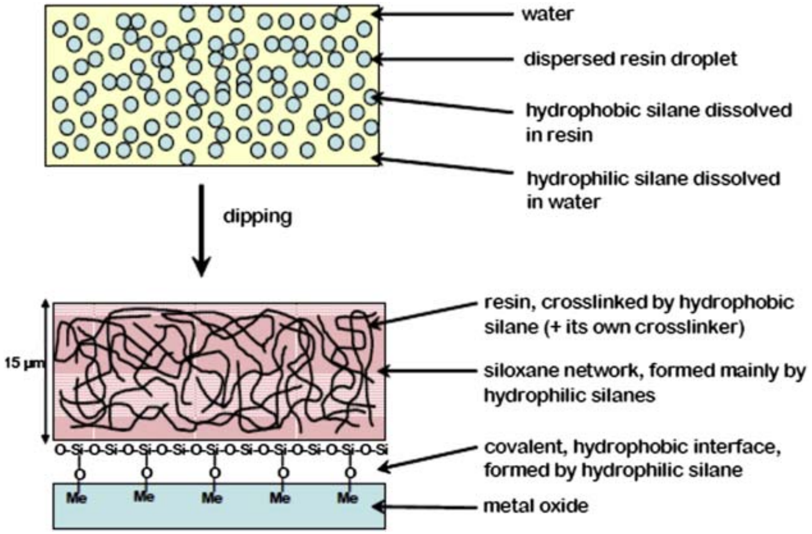


Figure 1.12 Schematic of the preparation of super primer [41].

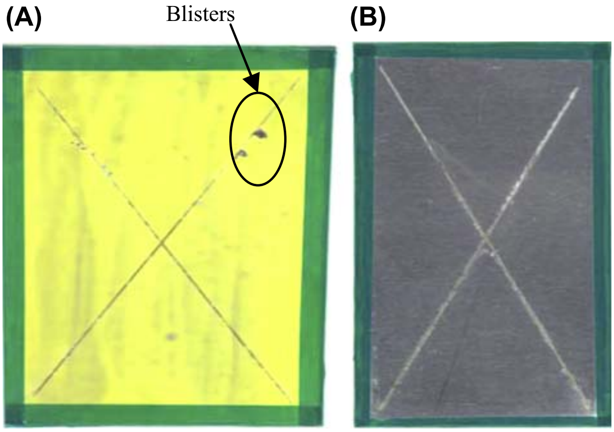


Figure 1.13 Painted AA 2024-T3 panels after 2 month of immersion in 3.5% NaCl solution; (A) painted with solvent-borne, chromated MIL-PRF-23377 epoxy primer and (B) painted with super primer with 10% nonhydrolyzed bis-sulfur silane [41].

chromated epoxy primer and also to eliminate the chromate conversion coating.

This enhancement effect is likely attributed to in situ hydrolysis and condensation of bis-sulfur silane molecules in the super primer and at the primer/metal surface during immersion in the 3.5% NaCl solution. Zhu [63] studied structural evolution of a partially cross-linked bis-sulfur silane coating on AA 2024-T3 when immersed in a 0.5 M K_2SO_4 aqueous solution by EIS and FTIR. The work revealed that during immersion, the remaining hydrolyzable groups ($-OC_2H_5$) in the bis-sulfur silane molecules undergo in situ hydrolysis to form silanols (Si—OH). These Si—OH groups further cross-link in situ to create a dense siloxane (Si—O—Si) network within the coating and also to react with Al hydroxyl groups (Al—OH) on the metal surface to form extra amounts of Al-O-Si bonds. The in situ formation of the siloxane network reduces the porosity of the coating, resulting in the enhanced physical barrier property (or water resistance) of the coating. The increased amount of Al-O-Si bonds formed at the interface also improves adhesion between the coating and the metal.

Schaefer et al. [42] studied the water resistance of the interfacial structure of silane-coated aluminum on Si wafer by XRR. In this work, bis-sulfur silane film and bis-amino silane film were spin-coated onto Al layer, which was deposited on a Si wafer, respectively. Heavy water (D_2O) was used for determining water absorption (volume fraction of D_2O, φ_{D_2O}) in both silane films. The resulting SLD profiles are shown in Fig. 1.14.

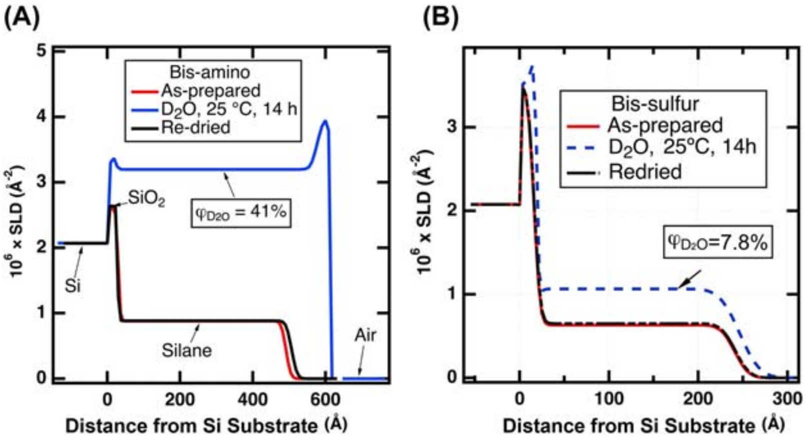


Figure 1.14 SLD profiles for bis-amino silane film (A) and for bis-sulfur silane film (B) spin coated on the Al layer that was deposited on a Si wafer [42].

These profiles were obtained assuming a layered model and then inverting neutron reflectivity data. Fig. 1.14A shows the SLD profile for bis-amino silane film. The SLD of the dry film (solid red curve: gray curve in print version) indicates the film is fully cross-linked. After exposure to D_2O vapor for 14 h, the blue curve (dark gray curve in print version) is obtained. The SLD of the swollen film is now much higher due to absorption of D_2O, whose SLD is six times higher than that of the dry film. The volume fraction φ of D_2O in the film is calculated from the SLD to be 41%. That is, 41% of the volume is occupied by D_2O even though the film swells by only 25%. This high water content is due to the hydrophilic nature of the secondary amino group (—NH—) in the bis-amino silane molecule. The film returns almost to the pristine state on redrying, showing that there is no chemical alternation due to water exposure at room temperature. Fig. 1.14B shows the SLD profile for bis-sulfur film that is hydrophobic, leading to less water absorption ($\varphi_{D_2O} = 7.8\%$) than bis-amino film ($\varphi_{D_2O} = 41\%$).

4. Conclusions

- Driven by strict regulations on the use of chromates and VOC/HAP in military coatings and by demand for improved lifetime of coated military assets, formulators are seeking new high-performance coatings that are also compliant with current health and environmental regulations. With its unique merits, sol–gel technology has become especially attractive to the formulators in recent years.

- The merits associated with sol—gel coatings include (1) process flexibility (e.g., ambient spraying or immersion application), (2) highly cross-linked coating structure, acting as an excellent physical barrier to retard the ingress of water/corrosive species, (3) covalent bonding to metals substrates to provide strong adhesion at metal/coating interface, and (4) the use of environmentally friendly sol—gel precursors.
- Water-based sol—gel coatings have been evaluated in military applications in two aspects: (1) water-based sol—gel pretreatment coatings as a replacement for chromate and phosphate pretreatments and (2) anticorrosive waterborne coatings enhanced by organofunctional trialkoxysilanes ("super primer") as a replacement for chromated epoxy primers.
- Organofunctional silane-based pretreatment coatings and zirconium oxide pretreatment coatings have demonstrated excellent paint adhesion and corrosion protection for painted metal substrates in many applications. However, their inherent drawbacks have been noticed in industrial applications. As a result, hybrid pretreatment coatings have emerged as a solution to overcome these drawbacks. These hybrid pretreatment coatings are formed by combining at least two different types of sol—gel precursors that contain organic and inorganic components.
- Research has indicated that anticorrosion performance of waterborne coatings can be enhanced by adding hydrophobic organofunctional silanes. This improvement is attributed to in situ silane hydrolysis and condensation in the coating triggered by exposure to aqueous media. Silanol groups generated from in situ hydrolysis cross-link to create a dense siloxane (Si—O—Si) network within the coating and also react with Al hydroxyl groups (Al—OH) on the metal surface to form extra amounts of metallosiloxane (Al—O—Si) bonds. The in situ formation of the siloxane network reduces the porosity of the coating, resulting in the enhanced physical barrier property (or water resistance) of the coating. The increased amount of metallosiloxane bonds formed at the interface also improves adhesion between the coating and the metal.

References

[1] M. Atik, P. Neto, L.A. Avaca, M.A. Aegerter, Ceram. Int. 21 (1995) 403.
[2] M. Atik, F.P. Luna, S.H. Messaddeq, M.A. Aegerter, J. Sol. Gel Sci. Technol. 8 (1997) 517.
[3] F. Perdomo, P.D. Lima, M.A. Aegerter, L.A. Avaca, J. Sol. Gel Sci. Technol. 15 (1999) 87.
[4] S.H. Messaddeq, S.H. Pulcinelli, C.V. Santilli, A.C. Guastaldi, Y. Messaddeq, J. Non-Cryst. Solids 247 (1999) 164.

[5] J. Masalski, J. Gluszek, J. Zabrzeski, K. Nitsch, P. Gluszek, Thin Solid Films 349 (1999) 186.
[6] L. Fedrizzi, F.J. Rodriguez, S. Rossi, F. Deflorian, R.D. Maggio, Electrochim. Acta 46 (2001) 3715.
[7] T.P. Chou, C. Chandrasekaran, G.Z. Cao, J. Sol. Gel Sci. Technol. 26 (2003) 321.
[8] H. Sayilkan, S. Sener, E. Sener, M. Sulu, Mater. Sci. 39 (2003) 733.
[9] T. Sugama, J. Coat. Technol. Res. 2 (October) (2005) 649.
[10] L. Jianguo, G. Gaoping, Y. Chuanwei, Surf. Coat. Technol. 200 (2006) 4967.
[11] A. Conde, J.D. Damborenea, A. Duran, M. Menning, J. Sol. Gel Sci. Technol. 37 (2006) 79.
[12] Y. Chen, L. Jin, Y. Xie, J. Sol. Gel Sci. Technol. 13 (1998) 735.
[13] N.N. Voevodin, N.T. Grebasch, W.S. Soto, L.S. Kasten, J.T. Grant, F.E. Arnold, M.S. Donley, Prog. Org. Coat. 41 (2001) 287.
[14] N. Voevodin, C. Jeffcoate, L. Simon, M. Khobaib, M. Donley, Surf. Coat. Technol. 140 (2001) 29.
[15] L.S. Kasten, J.T. Grant, N. Grebasch, N. Voevodin, F.E. Arnold, M.S. Donley, Surf. Coat. Technol. 140 (2001) 11.
[16] N.N. Voevodin, N.T. Grebasch, F.E. Arnold, M.S. Donley, Surf. Coat. Technol. 140 (2001) 24.
[17] Y. Joshua Du, M. Damron, G. Tang, H. Zheng, C.J. Chu, J.H. Osborne, Prog. Org. Coat. 41 (2001) 226.
[18] R.L. Parkhill, E.T. Knobbe, M.S. Donley, Prog. Org. Coat. 41 (2001) 261.
[19] N.N. Voevodin, V.N. Balbyshev, M. Khobaib, M.S. Donley, Prog. Org. Coat. 47 (2003) 416.
[20] A.N. Khramov, V.N. Balbyshev, N.N. Voevodin, M.S. Donley, Prog. Org. Coat. 47 (2003) 207.
[21] V. Palanivel, D. Zhu, W.J. van Ooij, Prog. Org. Coat. 47 (2003) 384.
[22] D. Zhu, W.J. Van Ooij, Corros. Sci. 45 (2003) 2177.
[23] S. Ono, H. Tsuge, Y. Nishi, S. Hirano, J. Sol. Gel Sci. Technol. 29 (2004) 147.
[24] A.N. Khramov, N.N. Voevodin, V.N. Balbyshev, M.S. Donley, Thin Solid Films 447 (2004) 549.
[25] A.N. Khramov, N.N. Voevodin, V.N. Balbyshev, R.A. Mantz, Thin Solid Films 483 (2005) 191.
[26] V. Palanivel, Y. Huang, W.J. van Ooij, Prog. Org. Coat. 53 (2005) 153.
[27] W. Datchary, A. Mehner, H.W. Zoch, D.A. Lucca, M.J. Klopfstein, R. Ghisleni, D. Grimme, E. Brinksmeier, J. Sol. Gel Sci. Technol. 35 (2005) 245.
[28] M.L. Zheludkevich, D.G. Shchukin, K.A. Yasakau, H. Mohwald, M. Ferreira, Chem. Mater. 19 (2007) 402.
[29] K.H. Wu, C.M. Chao, T.F. Yeh, Surf. Coat. Technol. 201 (2007) 5782.
[30] D. Wang, G.P. Bierwagen, Prog. Org. Coat. 64 (2009) 327.
[31] R.B. Figueira, I.R. Fontinha, C.J.R. Silva, E.V. Pereira, Coatings 6 (2016) 12, https://doi.org/10.3390/coatings6010012.
[32] J. Ouyang, US Patent No. 5,662,967, 1997.
[33] T. Matsuda, A. Matsuzaki, M. Sasaki, K. Takashima, US 2012/0088122 A1, 2012.
[34] M. Yujiro, T. Akira, M. Atsushi, Patent No. JP2004197179, 2004.
[35] T. Kolberg, M. Walter, P. Schubach, US Patent No: 8101014 B2, 2012.
[36] W. Claffey, J. McIntyre, L. Beck, US 20050022907 A1, 2005.
[37] A. Schmidt, N. Teubert, F. Czika, S. Cornen, US 8557096 B2, 2013.
[38] D. Zhu, W.J. Vanooij, US 8383204 B2, 2013.
[39] A. Seth, W.J. van Ooij, J. Mater. Eng. Perform. 13 (2004) 292.
[40] W.J. van Ooij, A. Seth, T. Mugada, G. Pan, D.W. Schafer, A novel self-priming coating for corrosion control, in: International Surface Engineering Congress and Exposition, ASM International, Orlando Florida, August 2–4, 2004.

[41] A. Seth, W.J. van Ooij, P. Puomi, Z. Yin, A. Ashirgade, S. Bafna, C. Shivane, Prog. Org. Coat. 58 (2007) 136.
[42] D.W. Schaefer, G. Pan, W.J. van Ooij, Los Alamos Sci. 30 (2006).
[43] W.J. van Ooij, A. Seth, M. B Stacy, US Patent No United States Patent 7732016, 2008.
[44] H. Kinder, et al., IEEE Trans. Appl. Supercond. 5 (2) (1995) 1575.
[45] R. Wördenweber, Supercond. Sci. Technol. 12 (1999) R86—R102.
[46] M. Kakihana, J. Sol. Gel Sci. Technol. 6 (1996) 7—55.
[47] J.D. Wright, N.A.J.M. Sommerdijk, Sol-Gel Materials: Chemistry and Applications, Gordon and Breach Science Publishers, Amsterdam, 2001.
[48] C.J. Brinker, G.W. Scherer, Sol—Gel Science: The Physics and Chemistry of Sol—Gel Processing, Harcourt Brace Jovanovich, Academic Press, Inc., Boston, 1990.
[49] A.L.K. Tan, A.M. Soutar, I.F. Annergren, Y.N. Liu, Surf. Coat. Technol. 198 (2005) 478.
[50] B. Veeraraghavan, B. Haran, D. Slavkov, S. Prabhu, B. Popov, B. Heimann, Electrochem. Solid State Lett. 6 (2003) B4.
[51] M. Sheffer, A. Groysman, D. Mandler, Corros. Sci. 45 (2003) 2839.
[52] Y. Castro, B. Ferrari, R. Moreno, A. Duran, J. Sol. Gel Sci. Technol. 26 (2003) 735.
[53] J. Wen, G.L. Wilkes, Chem. Mater. 8 (1996) 1667.
[54] L.L. Beecroft, C.K. Ober, Adv. Mater. 7 (1995) 1007.
[55] T. Materne, F. de Buyl, G.L. Witucki, Organosilane Technology in Coating Applications: Review and Perspectives, 2012. http://www.dowcorning.com/zh_CN/content/publishedlit/26-1402-01.pdf.
[56] E.P. Plueddemann, Silane Coupling Agents, second ed., Plenum Press, NY, 1991.
[57] A.J. Gellman, B.M. Naasz, R.G. Schmidt, M.K. Chaudhury, T.M. Gentle, J. Adhes. Sci. Technol. 4 (7) (1990) 597.
[58] E.P. Plueddemann, Reminiscing on silane coupling agents, in: K.L. Mittal, V.S.P. Utrecht (Eds.), Silane and Other Coupling Agents, 1992, p. 2. Netherlands.
[59] D. Zhu, W.J. van Ooij, Prog. Org. Coat. 49 (2004) 42.
[60] D. Zhu, W.J. van Ooij, Electrochim. Acta 49 (7) (2004) 1113.
[61] V. Subramanian, W.J. van Ooij, Corrosion 54 (3) (1998) 204.
[62] W.J. van Ooij, D. Zhu, M. Stacy, A. Seth, T. Mugada, J. Gandhia, P. Puomi, Tsinghua Sci. Technol. 10 (6) (2005) 639.
[63] D. Zhu, (Ph.D. dissertation), University of Cincinnati, 2005.
[64] F.W. Eppensteiner, M.R. Jenkins, Chromate conversion coatings, Met. Finish. 100 (Suppl. 1) (2002) 479—491.
[65] H.A. Katzman, G.M. Malouf, R. Bauer, G.W. Stupian, Corrosion-protective chromate coatings on aluminum, Appl. Surf. Sci. 2 (1979) 416—432.
[66] M. Kendig, S. Jeanjaquet, R. Addison, J. Waldrop, Surf. Coat. Technol. 140 (2001) 58.
[67] https://www.serdp-estcp.org/content/download/5746/79024/file/wp-0025%20IR.pdf.
[68] Gusmano, G. Montesperelli, M. Rapone, G. Padeletti, A. Cusma, S. Kaciulis, A. Mezzi, R. Maggio, Surf. Coat. Technol. 201 (2007) 5822P.
[69] Puomi, H.M. Fagerholm, J.B. Rosenholm, K. Jyrkäs, Surf. Coat. Technol. 115 (1999) 70.
[70] P. Puomi, H.M. Fagerholm, J.B. Rosenholm, R. Sipilä, Surf. Coat. Technol. 115 (1999) 79.
[71] P. Puomi, H.M. Fagerholm, A. Sopanen, Anti-corros. Meth. Mater. 48 (2001) 160.
[72] S. Verdier, S. Delalande, N. van der Laak, J. Metson, F. Dalard, Surf. Interface Anal. 37 (2005) 509.
[73] S. Verdier, N. van der Laak, F. Dalard, J. Metson, S. Delande, Surf. Coat. Technol. 200 (2006) 2955.

[74] S. Adhikaria, K.A. Unocica, Y. Zhaia, G.S. Frankela, J. Zimmermanb, W. Fristadb, Electrochim. Acta 56 (2011) 1912.

[75] N.J. Silvernail, J.L. Stalker, T. Lingenfelter, Environmentally Friendly Zirconium Oxide Pretreatment, 2013. https://www.serdp-estcp.org/content/download/21121/221351/file/WP-1676-FR.pdf.

[76] Y.J. Chung, S.L. Jeanjaquet, M.W. Kendig, US Patent No: 6,579,472 B2, 2003.

[77] K.Y. Blohowiak, J.W. Grob, J.H. Osborne, US Patent No: 8592042 B2, 2013.

[78] K.Y. Blohowiak, J.H. Osborne, J.E. Seebergh, SAE International Technical Paper 2009-01-3208, 2009. https://doi.org/10.4271/2009-01-3208.

[79] D. Zhu, W.J. Vanooij, W. Zhang, US Patent No: 8597482 B2, 2013.

[80] G. Pan, E. Watkins, J. Majewski, D.W. Schaefer, J. Phys. Chem. C 111 (2007) 15325.

[81] J. Kelley, T. Considine, T. Braswell, ARL-TR-7244, 2015. www.dtic.mil/get-tr-doc/pdf?AD=ADA620227.

[82] W.J. Vanooij, Wash Primer Replacement Based on the Superprimer Technology, 2011. https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Surface-Engineering-and-Structural-Materials/Coatings/WP-1675/WP-1675.