Novel Silane-Based pretreatments of Metals to Replace Chromate and Phosphate Treatment

In this program we are developing simple, one-step rinses with aqueous solutions of silanes for the metals cold-rolled steel, galvanized steel and aluminum. These treatments will be optimized so as to replace currently used chromate, phosphate and combined treatments in a wide range of metal-processing industries. The silane solutions consist of an organofunctional silane, a non-functional silane is different for each metal used. We are also studying the stability of the silanes in the solution, as our ultimate goal is to develop concentrated mixtures of the three components which can be diluted on site to result in an active aqueous solution. The treatment are cost-effective, do not involve toxic chemicals and produce only small amounts of waste.
Program Name:

Novel Silane-Based Pretreatments of Metals to Replace Chromate and Phosphate Treatments

Funding Agency:

National Risk Management Research Laboratory of the EPA (Cincinnati, Ohio); Category III Project, No. CR 822989-01-0 under Program: Physical/Chemical Technologies for Pollution Prevention and Waste Treatment

Short Description:

Project is aimed at developing new pretreatment rinses for metal surfaces in building, automotive, construction and beverage industries currently treated by phosphate or chromate-containing processes or both, prior to painting; all new rinses contain organofunctional silanes

Period:

October 1, 1994-September 30, 1997
Team

1. University of Cincinnati, Dept. of Materials Science and Engineering
   *PI: Wim J. van Ooij, Professor*

2. Four Ph.D. Graduate Students at UC, Dept. Of MS&E

   *Mr. George Górecki, Research Chemist*

4. Högskolan Dalarna, Borlänge, Sweden
   *Investigator: Sven-Erik Hömström, Assistant Professor*
PRINCIPLES OF SILICATE-SILANE RINSE OF PHOSPHATE

STEEL

0.005 M waterglass +
0.005 M Ca(NO₃)₂
pH = 12, T = 60°C, 30 s

[Zn, Ca]₂(OH)₆ [Zn, Ca]Si₂

STEEL

1% γ-APS, 20°C, 5 s

STEEL
ARMCO PATENTS ON SILICATE-SILANE PROCESSES
re-assigned to the University of Cincinnati

W.J. van Ooij, to Armco Inc., US Patent Appl., March 7, 1994, "Metal pretreated with an aqueous Solution containing a dissolved inorganic Silicate or Aluminate, an organofunctional silane and a non-functional Silane for enhanced Corrosion Resistance" (one-step treatment; in principle allowed)


W.J. van Ooij and A. Sabata, to Armco Inc., US Pat. 5,322,713, June 21, 1994, "Metal Sheet with Enhanced Corrosion Resistance having a Silane-treated Aluminate Coating"

W.J. van Ooij, R.A. Edwards and A. Sabata, to Armco, Inc., USP 5,292,549, March 8, 1994, "Metallic Coated Steel having a Siloxane Film Providing Temporary Corrosion Protection and Method Therefor"


Metals and Silanes

1. Metals

- Fe  \textit{model for CRS}
- Zn  \textit{model for EGS}
- Al  \textit{pure}

Galvalume (Al45Zn2Si) coatings on steel

2. Silanes

- $\gamma$-APS (all metals) \textit{aminopropylsilane}
- SAAPS (Fe and Galvalume) \textit{styrlyaminoethylaminopropylsilane}
- UPS (zinc) \textit{ureidopropylsilane}
- AEAPS ((Al only) \textit{diaminosilane}

3. Additives

- b-TESE \textit{bis-(triethoxysilyl)ethane (crosslinker)}
- silicate \textit{waterglass}

4. Treatments

Dip or spray in freshly hydrolyzed aqueous solution containing 1% silane, 0.2% crosslinker and 0.1% silicate; dry in air; variables are pH, ratios of components, and temperature
Project Flow Chart

METAL

Selection of Silanes

Corrosion of Metal in Aqueous Silane Solutions

pH = 3, 7, 10
Conc. = 0.1, 1, 10%
Age = 1, 24, 168 hrs

Reaction of Silane in Aqueous Solution

pH = 3, 7, 10
Conc. = 0.1, 1, 10%
Age = 0, 168, 4320 hrs

Dipping of Metal in Silane Solution

pH = 4, 7, 10
Conc. = 0.1, 1, 10%
Time = 1-10 min.

Corrosion of Dipped Metal

pH = 3, 7, 10
3% NaCl

Painting of Dipped Metal

Cathodic E-coat
Appliance Polyester
Automotive Topcoat
Powder Paint

Testing of Painted Metal

3% NaCl
168 hrs Salt Spray
4 wks Humidity

FINAL EVALUATION

DC EIS

FTIR

Ellipsometry
Contact Angle
RAIR
SIMS
XPS

Film Thickness
Homogeneity
Optical

EIS
ASTM B-117
GM 9540P
Methods used in Project

1. Characterization of Silane Solutions and Films

- Ellipsometry  
  Thickness of Film
- Electron Microprobe  
  Thickness and Homogeneity of Film
- Reflection-Absorption FTIR  
  Structure of Film
- Transmission FTIR  
  Reactions in Solution
- Time-of-Flight SIMS  
  Structure of Film
- X-Ray Photoelectron Spectroscopy (XPS)  
  Structure of Film
- Contact Angle Measurements  
  Surface Energy of Film

2. Performance of Treatments

- GM 9540P Scab Test  
  Corrosion after Painting
- Salt Spray Test  
  Corrosion after Painting
- DC and EIS Corrosion Tests  
  Corrosion before Painting
- Paint Pull-off Test  
  Adhesion
- Tape Adhesion Test  
  Adhesion
3. Analysis of Waste Streams

- ICP  
  Si, Fe and Zn
- AAS  
  Al
- GC  
  Methanol and Ethanol
Current Status

*Done in First Year of Project:*

1. Identified two suitable Silanes for each of the Metals Fe, Zn, Al
2. Studied the Structure of the Silane Films on these Metals
3. Developed appropriate Cleaning Methods for each Metal prior to Silane Application
4. Studied the Parameters that Control the Film Thickness for each Silane/Metal Combination
5. Studied the Stability of some Silanes in Aqueous Solution
6. Characterized by EIS a new commercial Silane Post-Rinse developed by Industrial Partner
7. Worked out a Licensing Agreement between UC and Brent America

*To be Done in Second Year of Project:*

1. Prepare large Number of Panels of CRS, EGS and Al by Treatment with Mixtures of selected Silanes, Crosslinker and Silicate
2. Have Panels painted by Brent America
3. Test Performance of Systems in Corrosion Test (GM Scab, GM 9540P) and Adhesion Test (ASTM D4541-93)
4. Have duplicate Systems Tested by Brent America in Corrosion Test (Salt Spray Test, ASTM B117-90) and Adhesion Test (Tape Test, ASTM D3359-90)
5. Arrange for Scale-up Experiments in Pilot Line at Brent America
Advantages of new Treatments

- Non-toxic Chemicals
- Improved Adhesion to Paints
- Flexibility in Choice of Silane for specific Metal
- No Final Water Rinse necessary
- Low Concentrations in Waste Streams
- Inexpensive Chemicals and very thin Films
Summary of Results

on

Stability of Silane Solutions and Characterization of Silane Films on Iron Substrate
(from September 1994 to September 1995)

Silanes and Additives Studied: $\gamma$-aminopropyltriethoxysilane ($\gamma$-APS), triaminofunctional silane (TAPS), a silane crosslinker-bis(triethoxysilyl) ethane (BTEE), and water glass

Substrate Used: Polished Pure Iron Coupon

Stability of Silane Solutions
(by visual Observation. Clear means stable, turbid means unstable)

Results of Stability Tests

<table>
<thead>
<tr>
<th>Silane Solutions</th>
<th>pH</th>
<th>Time of Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8% $\gamma$-APS, 0.2% BTEE and 0.005M water glass</td>
<td>5.0</td>
<td>&gt; 4 months, clear</td>
</tr>
<tr>
<td>8% $\gamma$-APS, 2% BTEE, and 0.05M water glass</td>
<td>5.0</td>
<td>&gt; 4 months, clear</td>
</tr>
<tr>
<td>0.5% $\gamma$-APS and 0.5% BTEE</td>
<td>9.0</td>
<td>immediately, turbid</td>
</tr>
<tr>
<td>8% $\gamma$-APS, 2% BTEE, and 0.05M water glass</td>
<td>6.0</td>
<td>&gt; 3 months, clear</td>
</tr>
<tr>
<td>0.8% $\gamma$-APS, 0.2% BTEE and 0.005M water glass</td>
<td>9.0</td>
<td>&gt; 2 months, clear</td>
</tr>
</tbody>
</table>

Conclusion:

* A stable solution of $\gamma$-APS+Y9805+water glass which was stable for at least 4 months can be prepared under certain pH and concentration conditions.
Characterization of Silane Films on Iron Substrate


Conclusions:

1. The hydrolyzed APS film on iron is not stable and reacts with air upon aging.

2. The thickness of APS and BTEE is a function of concentration and pH.

3. The thickness is independent of dipping time.

4. The structure of mixtures of APS and BTEE with 4 to 1 ratio is influenced by pH but not by concentration, and dominated by the contribution from APS.

5. Drying technique affects the structure, orientation, and thickness of silane films on Fe.

6. High dipping temperature results in the increase in the thickness.

7. Heating of silane films at elevated temperature increases the crosslinking.
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Substrate:
- Zinc ⇒ Galvanized Steel

Silane Studied:
- Gamma Aminopropyltriethoxysilane (γ-APS)
- Gamma Mercaptopropyltrimethoxysilane (γ-MPS)
- Gamma Ureidopropyltrialkoxy silane (γ-UPS)
- Mixture of Silane, 1,2-Bis(triethoxysilyl) Ethane (TESE) and Sodium Silicate

Characterization Techniques:
- Ellipsometry
- Surface Energy Measurements
- Reflection Absorption Infrared Spectroscopy (RAIR)
- Time-of-Flight Secondary Ion Mass Spectroscopy (TOFSIMS)

Deposition Parameters:
- Solution Concentration
- Solution Dipping Time
- pH Value of the Solution

Conclusions:
- Film thickness depends on solution concentration but independent of solution dipping time
- Molecular Orientation depends on pH value of the solution
- Surface energy decrease with the film aging time
Bio-Rad Win-IR.

γ-UPS Mixture on Polished Zinc Substrate

γ-UPS on Polished Zinc Substrate

γ-UPS Monomer

View Mode: Overlay

# 1 : UPS6262S

Number of Scans: 128

Annotation: ups on zinc

6/26/95 1:15 PM Res=4cm-1
Fig. 1  Effect of solution concentration on the film thickness of APS and UPS coated zinc substrates (solution dipping time = 1 minute).
Fig. 2 Effect of solution dipping time on the film thickness of APS and UPS coated zinc substrates (solution concentration = 1%, by volume).
Effect of film aging time on the surface energy of 1% MPTS coated pure zinc substrate (solution aging time is 20 hrs.).
The influence of deposition parameters on Al

- **Solution concentration**
  concentration increases, silane film thickness increases

- **Al dipping time**
  in a short duration, it does affect the silane film thickness (<2 min.)

- **pH value**
  it depends on the parameters to hydrolysis and condensation process of silane solution, pH around 8 is best to get good film

- **Aging time**
  surface tension decreases with aging time, it becomes constant after about 3-4 days

- **Cleaning steps**
  DI water and acetone ultrasonic clean (5 min. each)

- **Temperature**
  from 20°C to 100°C increasing the film extent of crosslinking, above 200°C film degrades
Corrosion Inhibition of Iron by γ-APS

FACTORS INFLUENCING CORROSION

* pH
* Solvent
* Aging of the solution
* Curing time
* Silane concentration
* Dipping time
* Curing temperature

RESULTS

* pH controls the mode of attachment
  
  through the amino end at high pHs
  through the silane end at lower pHs

* Solvent to be chosen based on pH of application
  
  alcohols prevent etching at low pHs

* Curing temperature/Time
  
  60 °C–60 minutes found to be ideal

* Aging of the solution results in condensation of the silane

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Deposited after condensation
before condensation
Fig. 1 Corrosion rates as a function of pH
Related Activities

Deposition of thin Organic Coatings on Metals by Polymerization of Organic Monomers in a DC Plasma

Advantages:

- Process is Solvent-free
- Process is very Efficient and requires very little Energy (e.g. 0.05 W/cm²)
- Coatings can be tailored to specific Substrates and Applications (Choice of Deposition Conditions and Monomer)
- Coatings outperform Phosphates and Chromates in some Applications
- Coatings are thermally very stable and insoluble in Solvents
- Coatings with a high Degree of Deformability can be obtained
- In Situ Cleaning and Deposition in Sequential Steps
2nd Annual
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An Information Exchange

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Seven Springs Mountain Resort
Champion, PA