Light metal corrosion protection with water-borne silane systems

Dr. Philipp Albert
14.06.2011
1. Silanes, hydrolysis and condensation, sol-gel process

2. Water-borne sol-gel systems

3. Dynasylan® SIVO 160

4. Possible applications of SIVO 160 formulations on aluminium

5. Applications on magnesium

6. Summary
Evonik’s production plants for organofunctional silanes
Most commercial organofunctional silanes feature the same molecular formula.

Organofunctional group can react with polymers, resins, rubber,…

Silicon-functional group can react with fillers, metals, glass,…

Non hydrolyzable

Hydrolyzable
Silanes, hydrolysis and condensation

OR = “Silicon-functional“ group
Y = “Organofunctional“ group

Polymer + Silane + Surface

Adhesion promotion

14.06.2011
Dr. Philipp Albert
Hydrolysis of alkoxy groups: Reactivity of silanes/silanols

- pH-Value
- Concentration
- Type of catalyst
- Solvent
- Temperature
- Organofunctional group: Y
- Si-functional group: OAc > OMe > OEt

![Graph showing reactivity of silanes/silanols](chart)

- Y-(CH₂)₃-Si(OR)₃

- OH⁻ - catalyzed
  - Fast gelation (highly branched products)

- H⁺ - catalyzed
  - Slow gelation (linear products)
Condensation – Influence of the pH-value

Monomer → Dimer → Cyclic

Acidic solution: Linear and branched structures
Alkaline solution: Highly branched structures
Sol-gel process

Animation
1. Silanes, hydrolysis and condensation, sol-gel process

2. Water-borne sol-gel systems

3. Dynasylan® SIVO 160

4. Possible applications of SIVO 160 formulations on aluminium

5. Applications on magnesium

6. Summary
Five generations of functional silanes developed by Evonik Degussa

- **Traditional Silanes**
  - Dynasylan® VTMO
  - AMEO

- **Special Silanes**
  - Dynasylan®
    - 1189
    - 4148
    - 1124

- **Low VOC Oligomeric Silanes**
  - Dynasylan®
    - 9896
    - 1146

- **Water-Borne Silanes**
  - HYDROSIL
    - 2627
    - 2909

- **Water-Borne Sol-Gel Technology**
  - SIVO® SOL Technology

The timeline shows the development of these silanes from 1970 to 2010.
Modification of water-borne sol-gel systems

Different silanes used in the hydrolysis and co-condensation process open up the way for water-borne sol-gel systems. Hydrophilic, hydrophobic and adhesion properties as well as the curing temperature can be varied within a certain range.

\[
\begin{align*}
R\text{—}\text{Si(OR')}_3 & \\
X\text{—}\text{Si(OR')}_3
\end{align*}
\]

\[
\begin{align*}
\text{HO—Si—O—H} & \\
\text{X—Si—O—H}
\end{align*}
\]

R = hydrophobic, X = hydrophilic group
Advantages:

• Water-borne, VOC-free

• Long shelf-life

• Temperature curing

• Different applications possible (primer, additive, binder)

• Environmentally friendly
Agenda

1. Silanes, hydrolysis and condensation, sol-gel process

2. Water-borne sol-gel systems

3. Dynasylan® SIVO 160

4. Possible applications of SIVO 160 formulations on aluminium

5. Applications on magnesium

6. Summary
Dynasylan® SIVO 160 – A new water-borne low temperature curing sol-gel system

Key properties

- Water-borne
- Nearly VOC-free
- Shelf life time of 1 year
- pH ~ 4.0 – 4.6
- Solid content ~ 9 %
- Colorless to yellow liquid
- Viscosity 9.1 mPa s (20 °C)
The amount of silanol groups and the degree of branching of Dynasylan® SIVO 160 can be measured via $^{29}$Si-NMR spectroscopy.
Dynasylan® SIVO 160 – particle size of the sol

Particle distribution of Dynasylan® SIVO 160
Volumetric median particle size: 5.4 nm
Example for the high reactivity of Dynasylan® SIVO 160

- Dynasylan® SIVO 160 is highly reactive
- Droplets of Dynasylan® SIVO 160 that remain inside the top of the bottle will get solid due to evaporation of water
- Due to the reactivity, formulations with a high filler load are difficult
Agenda

1. Silanes, hydrolysis and condensation, sol-gel process
2. Water-borne sol-gel systems
3. Dynasylan® SIVO 160
4. Possible applications of SIVO 160 formulations on aluminium
5. Applications on magnesium
6. Summary
Sol-gel systems for metal protection

Key benefits of silane systems

- Barrier protects against water and chloride
- Hydrophobic surface layer
- Better adhesion of subsequent coating
- Reaction with surface enables some passivation

Passivation of metal surface due to reaction with substrate
**Dynasylan® SIVO 160 on aluminum substrate**

<table>
<thead>
<tr>
<th>Aluminium substrate</th>
<th>Coated aluminum substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Aluminium substrate" /></td>
<td><img src="image" alt="Coated aluminium substrate" /></td>
</tr>
<tr>
<td>SIVO 160 1. Dipping 2. Curing 80 °C</td>
<td>Layer thickness ~ 50 - 150 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Investigation of the surface via XPS</th>
<th>Si*</th>
<th>0.89</th>
<th>19.6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al*</td>
<td>33.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

* [atom %]

---

10 % aqueous solution of Dynasylan® SIVO 160 coats aluminium substrate without defects
Application of Dynasylan® SIVO 160 on different aluminium alloys

**Substrate:**
- Aluminium alloy 2024 clad / 5005

**Decreasing/Cleaning:**
- Alkaline solution
- Acid pickling for alloy 5005

**Application:**
- Dipping in SIVO 160 dilution or SIVO 160 formulation
- Curing at 80 °C (10 min)

**Formulation in H₂O:**
- 12,5 % SIVO 160
- 0,02 % wetting agent
- 600 ppm Cr³⁺
Dynasylan® SIVO 160 for blank corrosion protection on aluminium 2024 clad

600 hours NSS

Blank

SIVO 160 dilution

SIVO 160 formulation

Corrosion

No corrosion

No corrosion

Dry layer thickness: ~ 100 – 200 µm
Dynasylan® SIVO 160 for blank corrosion protection on aluminium 5005

<table>
<thead>
<tr>
<th>1000 hours NSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank 5005</td>
</tr>
<tr>
<td>Corrosion</td>
</tr>
</tbody>
</table>

Blank 5005 formulation

SIVO 160 dilution

Cr(III) solution

Corrosion

No corrosion
Blank corrosion protection of Dynasylan®
SIVO 160 formulation on aluminum 5005

1000 h NSS

Blank
SIVO 160 formulation
Chromated

Pitting corrosion
No pitting corrosion
Little pitting corrosion
Corrosion protection on aluminum alloy 5005 with coil coating system

**Substrate:**
- Aluminum (5005)

**Cleaning:**
- Alkaline degreasing
- Alkaline etching
- Acid pickling

**Pre-treatment:**
- SIVO 160 formul.
- Pre-dried at 60 °C 10 min

**Topcoat:**
- Coil coating
  a) Primer
  b) Top coat
- PMT 232 °C
1. Silanes, hydrolysis and condensation, sol-gel process

2. Water-borne sol-gel systems

3. Dynasylan® SIVO 160

4. Possible applications of SIVO 160 formulations on aluminium

5. Applications on magnesium

6. Summary
Corrosion protection on magnesium - Cleaning procedure

The cleaning procedure is most important for the performance of Dynasylan® SIVO 160

Substrate:
- Magnesium (AZ31B)

Degreasing/Cleaning:
- Alkaline degreasing and acid pickling
  or
- Alkaline degreasing

After cleaning

<table>
<thead>
<tr>
<th>Alkaline degreasingacid pickling</th>
<th>Alkaline degreasing</th>
</tr>
</thead>
</table>
Corrosion protection on magnesium with polyester powder coating

**Substrate:**
- Magnesium (AZ31B)

**Degreasing/ Cleaning:**
- Alkaline degreasing
- Acid pickling

**Pre-treatment:**
- SIVO 160
- Pre-dried at 60 °C, 10 min

**Topcoat:**
- Polyester powder coating, 60 μ
- Cured at 180 °C, 20 min
Corrosion protection on magnesium with polyester powder coating

Substrate:
- Magnesium (AZ31B)

Degreasing/ Cleaning:
- Alkaline degreasing

Pre-treatment:
- SIVO 160 solution
- Pre-dried at 60 °C, 10 min

Topcoat:
- Polyester powder coating, 60 µ
- Cured at 180 °C, 20 min

Dynasylan® SIVO 160 works best after alkaline degreasing
## Product range: Water-borne silanes and binder systems

### Stability in dilute aqueous solution at pH

<table>
<thead>
<tr>
<th>Dynasylan®</th>
<th>Functionality</th>
<th>Solid content [%]</th>
<th>pH-Value</th>
<th>Stability* in dilute aqueous solution at pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>3 - 5</td>
<td>6 - 8</td>
</tr>
<tr>
<td>HYDROSIL 2627</td>
<td>Amino/alkyl/silanol</td>
<td>20</td>
<td>10 – 11</td>
<td>✓</td>
</tr>
<tr>
<td>HYDROSIL 2776</td>
<td>Diamino/alkyl/silanol</td>
<td>25</td>
<td>10 – 11</td>
<td>✓</td>
</tr>
<tr>
<td>HYDROSIL 2909</td>
<td>Amino/alkyl/silanol</td>
<td>37</td>
<td>4 – 5</td>
<td>✓</td>
</tr>
<tr>
<td>HYDROSIL 2926</td>
<td>Hydroxy/silanol</td>
<td>30</td>
<td>4 – 5</td>
<td>✓</td>
</tr>
<tr>
<td>SIVO 112</td>
<td>Fluoro/alkyl/amo/silanol</td>
<td>15</td>
<td>4 – 5</td>
<td>✓</td>
</tr>
</tbody>
</table>

### Advanced water-borne systems:

<table>
<thead>
<tr>
<th></th>
<th>Functionality</th>
<th>Solid content [%]</th>
<th>pH-Value</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIVO 110</td>
<td>Diol/SiO₂ particles/silanol</td>
<td>36</td>
<td>4 – 5</td>
<td>✓</td>
</tr>
<tr>
<td>SIVO 160</td>
<td>Amino/silanol</td>
<td>9</td>
<td>4 – 5</td>
<td>✓</td>
</tr>
</tbody>
</table>

* at least 3 months
Evonik’s value preposition within value chain

Evonik Degussa

Formulator

Applicator

End customer

Provides new base high performance silanes and silane binder systems SIVO® SOL Technology, e.g., SIVO 160, SIVO 110

Tailors high performance metal treatment systems to difficult end-use applications, e.g., electronics, automotive
1. Silanes, hydrolysis and condensation, sol-gel process

2. Water-borne sol-gel systems

3. Dynasylan® SIVO 160

4. Possible applications of SIVO 160 formulations on aluminium

5. Applications on magnesium

6. Summary
Summary

• Dynasylan® SIVO 160 is a water-borne nearly VOC-free and stable sol-gel systems with low curing temperature

• Blank corrosion protection on aluminium can be improved with special formulations

• Water-borne sol-gel systems can work as adhesion promoters on aluminium and magnesium

• The cleaning procedure of the metal substrates is important and will influence the corrosion protection performance of silanes or water-borne sol-gel systems
Dynasylan® brochures/ contact us

More information: http://www.dynasylan.com
or philipp.albert@evonik.com