Advanced Low Energy Coatings

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Technology Manager: Sol-gel
TWI

TWI Webinar
17th May 2012
Scope

- TWI
- Industrial context
- Background to surface energy
- Commercial low energy coating market
- Comparison of selected current products
- Next generation low energy coatings
- Conclusions
TWI – An extension to your resources

• Research & Technology organisation
• Membership based
• Effectively owned and run by members
  – TWI Council (appoints Exec Board)
  – Research Board
• Non-profit distributing and Limited by guarantee
**TWI supports industry**

- **Added value through**
  - Multidisciplinary support for customers projects
  - Supported by on-going, leading edge, research programme
  - Delivery of Innovation

- **Guarantee**
  - Impartial Service
  - Confidentiality
Examples of fouling

Biofouling on a ships hull

Ice build-up on buildings
Examples (2)

Heat exchangers

Aerospace

Heaters

Context

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Examples (3)

Oil & gas

Graffiti

Context
Examples (4)

Power distribution lines
Industrial context

- Fouling of surfaces
  - increases weight
  - causes drag
  - reduces flow
  - contaminates
  - provides sites for corrosion
  - reduces efficiency
  - increases emissions
  - demands cleaning
  - increases maintenance penalty

......COSTS MONEY
Industrial costs of fouling

- Wind turbines
  - Up to 25% reduction in power output
- Marine
  - 40% greater fuel consumption without anti-fouling treatments
- Heat exchangers
  - 0.25% GDP loss in industrialised nations
- Road transport
  - 10% increase in fuel consumption due to increased aerodynamic drag
- Oil & Gas
  - $40M per incident of plugged pipeline
Case Study: Wind Turbines

- Needs
  - Resistance to fouling
  - Ice/insect build up can reduce efficiency
  - Durability to erosion / wear
  - In-mould or post-mould coating application
  - Re-application in-situ
  - No acceptable commercial products available


Context
**Power: Wind Turbines**

**Context**

- Fouling can cause significant loss of efficiency
  - 25% reduction in power generation
  - Icing
  - Insect debris

**In Yukon (on-shore)**

10% of available production lost due to icing (150 kW, 10 m)
Potential Solutions

- Black blades – insufficient solar radiation at high latitudes
- Hot air blowers - €80/kW expensive
- Foil based heaters
  - Goodrich/Kelly/o2VK
- Low energy coatings
  - Insufficient anti-icing capability
  - Insufficient erosion durability
Background to surface energy

• Fouling occurs due to the build up of unwanted solid on a surface
  – Precipitation
  – Solidification
  – Biofouling

• Surface/liquid/ foulant compatibility

• Good interaction promotes good compatibility
• Poor wetting reduces compatibility and adhesion
• Low surface energy gives rise to poor wetting
Contact Angle

\[ Y_S = Y_L \cdot \cos \theta + Y_{SL} \]

Young Equation

\[ \cos \theta_w = r\cos \theta_c \]

Wenzel Equation

Liquid-solid interactions
- Polarity
- Electrostatic forces
- Hydrogen bonding

Contact angle is used as the primary measure of performance
**Wetting behaviour**

- **Non-wetting** → **Wetting**

- **Surface energy**

- **θ**

- **Puddle Depth**
Definitions

• Superhydrophilic $\theta < 35^\circ$

• Hydrophobic $\theta > 90^\circ$

• Superhydrophobic $\theta > 150^\circ$
## Chemical considerations

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\gamma_c$ (mN/m)</th>
<th>WCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptafluorodecyltrichlorosilane</td>
<td>12.0</td>
<td>120°</td>
</tr>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>18.5</td>
<td>115°</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>31.0</td>
<td>108°</td>
</tr>
<tr>
<td>Aluminium (3003 H14)</td>
<td>49</td>
<td>60°</td>
</tr>
<tr>
<td>Steel (A1008)</td>
<td>60</td>
<td>53°</td>
</tr>
<tr>
<td>Glass (dry)</td>
<td>78</td>
<td>&lt;15°</td>
</tr>
<tr>
<td>Tin oxide</td>
<td>111</td>
<td>&lt;5°</td>
</tr>
</tbody>
</table>
Commercial low energy coatings

- Market size at present $1–3Bn

- Based on chemical repulsion
  - maximum WCA 115° - 120°

- Dominant technological approaches
  - Fluorinated polymers - Teflon®
  - Fluorinated sulphonates - Scotchgard
  - Siloxanes/silicones - Silres®

- Future technical offerings
  - Silazanes - Tutoprom®
  - Inorganic-organic hybrids - Interlotus
Key products and companies

- BASF Hydrozo
- Wacker Silres
- DuPont Teflon
- 3M Scotchgard
- Solexis Hyflon
- AZ-EM Tuto-Prom
- Interlotus
- AcuIon
- Asahi Guard ESERIES
- Si-O

Fluoropolymer

Si-O Hybrid

Market
Characteristics of low energy coatings

Beneficial Properties
- Good adhesion
- Chemical/moisture resistance
- Corrosion/stain resistance
- Dirt/soil resistance
- Stability
- Easy to clean
- Enhanced release properties
- Grease/oil resistance
- Heat resistance
- Low surface energy
- UV resistance

Additional Attributes
- Anti-fog
- Anti-microbial
- Anti-static
- Fire retardancy
- Improved flow, gloss, clarity, etc.
- Low refractive index
- Non-stick characteristics
- Smoother finishes
- Vapor permeability

Market
<table>
<thead>
<tr>
<th>Feature</th>
<th>Silane / Siloxane</th>
<th>Fluoropolymers</th>
<th>Hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durability</td>
<td>Short/medium</td>
<td>Medium/long</td>
<td>Medium/long</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>Good</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Temperature resistance</td>
<td>Good</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Solvent based</td>
<td>-</td>
<td>Yes</td>
<td>-</td>
</tr>
<tr>
<td>Gas permeable</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Application considerations</td>
<td>Simple</td>
<td>Difficult</td>
<td>Simple</td>
</tr>
<tr>
<td>Cost</td>
<td>Med/high</td>
<td>High</td>
<td>Med/high</td>
</tr>
</tbody>
</table>
Overview of current products

• Fluoro-polymers
  – Dominant but are fundamentally limited
  – Legislation raises questions over long term viability
  – They are thermoplastic and therefore soft and easily abraded.

• Polysiloxanes
  – Soft and hydrophobic
  – Or hard, brittle and thickness sensitive with little hydrophobic character
Overview of current products

• Hybrids:
  – Currently solvent based
  – Thickness sensitive
  – Lack mechanical robustness
  – Niche applications
  – Hydrophobic and super-hydrophobic products available
  – Emergent technology
    – Related to high performance hard-coat technology
    – Potential for chemical manipulation to integrate with existing coatings
    – Low TRL but aimed at addressing limitations of conventional approaches
## Key players and existing products

<table>
<thead>
<tr>
<th>Product/Description</th>
<th>Teflon</th>
<th>Intersleek</th>
<th>Silres</th>
<th>TutoProm</th>
<th>Silicone Hardcoats</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produced by</td>
<td>DuPont</td>
<td>AkzoNobel Corporate</td>
<td>Wacker Silicones</td>
<td>Clariant / AZ-EM</td>
<td>Momentive Performance Materials</td>
</tr>
<tr>
<td>Company Sizes (2009)</td>
<td>€21,167m</td>
<td>€13,893m</td>
<td>€3,719m</td>
<td>€4,930m</td>
<td>€1,689m</td>
</tr>
<tr>
<td>Chemical Family</td>
<td>Fluorinated polymers</td>
<td>Fluorinated polymers</td>
<td>Silicones</td>
<td>Silizanes</td>
<td>Silicones</td>
</tr>
</tbody>
</table>
## Product comparison

<table>
<thead>
<tr>
<th>Feature</th>
<th>Teflon AF 900</th>
<th>Intersleek 900</th>
<th>Silres SY300</th>
<th>TutoProm</th>
<th>Silicone Hardcoats</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble in selected solvents</td>
<td>Biocide-free</td>
<td>Durable and flexible</td>
<td>Solvent-free</td>
<td>Protective effect for painted surfaces</td>
<td>Resistance to UV radiation for coloured polycarbonate, -</td>
</tr>
<tr>
<td>High gas permeability</td>
<td>Good resistance to mechanical damage</td>
<td>High resistance to aggressive atmospheric effects,</td>
<td>Anti-graffiti</td>
<td>Easy-to-clean</td>
<td>Resistance to microcracking,</td>
</tr>
<tr>
<td>High compressibility</td>
<td>Good colour retention</td>
<td>Good gloss retention</td>
<td>Colour fastness</td>
<td>Resistance to abrasion</td>
<td>Mar and thermal resistance</td>
</tr>
<tr>
<td>High creep resistance</td>
<td>Reduces the cost of vessels maintenance</td>
<td></td>
<td></td>
<td></td>
<td>Not hydrophobic</td>
</tr>
<tr>
<td>Low thermal conductivity</td>
<td>Antifouling</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low dielectric constant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**Market**

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## Comparative analysis (SWOT)

<table>
<thead>
<tr>
<th></th>
<th>Teflon AF</th>
<th>Intersleek 900</th>
<th>Silres SY300</th>
<th>TutoProm</th>
<th>Silicone Hardcoats</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S</strong></td>
<td>Recognised brand  &lt;br&gt;Well established supply chain  &lt;br&gt;International presence</td>
<td>industry benchmark for quality  &lt;br&gt;Sustainable growth  &lt;br&gt;Biocide-free  &lt;br&gt;Durability  &lt;br&gt;Energy-efficiency</td>
<td>Ease of application  &lt;br&gt;Good chemical resistance  &lt;br&gt;Low cost</td>
<td>Leader of protective coating for anti-vandalism</td>
<td>Long-term protection  &lt;br&gt;Versatile use  &lt;br&gt;UV protection</td>
</tr>
<tr>
<td><strong>W</strong></td>
<td>Unable to focus on niche market  &lt;br&gt;Easily damaged</td>
<td>highly specific industrial use</td>
<td>Short-term coating longevity</td>
<td>Limited applicability  &lt;br&gt;Thickness  &lt;br&gt;Solvent based</td>
<td>Solvent based  &lt;br&gt;Slow cure</td>
</tr>
<tr>
<td><strong>O</strong></td>
<td>Emerging markets  &lt;br&gt;(i.e. Asia Pacific and EE)  &lt;br&gt;Environmentally friendly</td>
<td>Production cost reduction</td>
<td>Building environmental control</td>
<td>Expand within emerging markets  &lt;br&gt;New applications</td>
<td>Renewable energy market  &lt;br&gt;New substrates, e.g. composites</td>
</tr>
<tr>
<td><strong>T</strong></td>
<td>Availability of close substitutes  &lt;br&gt;POP related health concerns</td>
<td>New entrants with lower prices</td>
<td>New entrants with lower costs</td>
<td>New additives integrated into existing paints</td>
<td>Legislation  &lt;br&gt;Rapid cure products</td>
</tr>
</tbody>
</table>

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Supply Chain

Raw materials
Building blocks
Formulators
Applicator
End user

Dow Corning • Evonik • Wacker • Shin-Etsu • Sartomer
• Momentive • Gelest
• Air Products • BASF • Bayer MS • Cytec • Degussa • Dow • Huntsman • Momentive • etc
DuPont
BASF
PPG
Bayer MS
Clariant
Akzo
Nobel
Cytec
e tc
Amtico
Carclo
Bombardier
GKN
Lockheed
GE
e tc
Mercedes
Airbus
Nokia
Siemens
GKN
Boeing
Caterpillar
e tc

Market

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Market Participants In Supply Chain

Additives
- Raw Materials & Building blocks: Evonik, Wacker, BASF, Momentive

Formulators
- DuPont, Akzo-Nobel, BASF, 3M, Evonik, Wacker, Whitford

Applicators
- Sinclair Optics, GKN

End Users
- GE, Lockheed
## Case study 2: Fluoropolymer company

<table>
<thead>
<tr>
<th><strong>Strengths</strong></th>
<th><strong>Opportunities</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>- Dominant technology</td>
<td>- Asia Pacific &amp; Eastern Europe</td>
</tr>
<tr>
<td>- Diverse product range</td>
<td>- Environmentally friendly</td>
</tr>
<tr>
<td>- Teflon brand recognition</td>
<td></td>
</tr>
<tr>
<td>- Well-established supply chain</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Weaknesses</strong></th>
<th><strong>Threats</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>- Focused on fluoropolymers</td>
<td>- New, high-tech coating companies</td>
</tr>
<tr>
<td>- PFOA/PFOS hazards</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Durability</td>
</tr>
</tbody>
</table>

**Market**
## Case study 3: Hybrid coating company

### Strengths
- Brand recognition
- Transportation sector contracts (Deutsche Bahn)
- Ambient temperature application

### Weaknesses
- Complex manufacturing process
- Single technology focus

### Opportunities
- Anti-Graffiti → Niche market
- Emerging polysilazanes (est. $93m USD)

### Threats
- Direct competition with alternative products e.g.
  - Evonik – Protectosil
  - 3M – anti-Graffiti window screen

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**Market**

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Mid sized fluoropolymer coating company
- PFOA and PTFE free
- Sol-gel based
- Consumer product
- Marks the transition to new synthesis technologies
Market drivers

- Environmental legislation
  - VOC (Volatile organic compounds 2004/41/CE)
  - POP (Persistent organic pollutants – Stockholm convention)
  - Carbon emissions reduction
  - Urban water run off – EPA

- Price increases for energy
  - Operational efficiency
  - Productivity
  - Maintenance
Comparison of inorganic-organic hybrids

- A range of products have been tested
- All were solvent based, easy to deposit and readily cured (ambient)
- Water contact angle typically between 74° and 104°
Background chemistry

Silica network formation via sol-gel reactions

**HYDROLYSIS:**

\[
\text{RO} + \text{Si-OR} + \text{HOH} \rightarrow \text{H_2O} + \text{Si-OR} + \text{RO}
\]

**CONDENSATION:**

\[
\text{Si(OH)} + \text{H_2O} \rightarrow \text{Si-OR-OR} + \text{OH}_2
\]

Comparison

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Sol-gel: Structural evolution


Where \( \text{Si(OR)}_x \text{(OH)}_y \text{(OSi)}_z \) is represented by \((X,Y,Z)\)

Comparison
Comparative study

- Deposit and cure on aluminium substrates
- Use water contact angle as the primary measure of performance
- Abrade and measure contact angle as a function of degree of abrasion
- Four silane treatments
- Four commercial products
- Two silica-silane hybrids
Comparison of aluminium coated samples

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Monolayer silanes</td>
</tr>
<tr>
<td>5-11</td>
<td>Commercial products</td>
</tr>
<tr>
<td>12-13</td>
<td>Silica-silane hybrid</td>
</tr>
</tbody>
</table>
**Abrasion resistance on aluminium**

Change in water contact angle after 500 double rubs with lint free cloth - aluminium substrate

Samples 1-4 Monolayer silanes
Samples 5-11 Commercial products
Sample 12-13 Silica-silane hybrid
Abrasion resistance on aluminium

Change in water contact angle after 500 double rubs with 0000 wire wool - aluminium substrate

Samples 1-4 Monolayer silanes
Samples 5-11 Commercial products
Sample 12-13 Silica-silane hybrid
Wear damage after 10 double rubs

Comparison

Silane

Commercial 1

Commercial 2

Commercial 3

Commercial 4

Hybrid

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Conclusion of comparison study

• A novel test routine which compares the hydrophobic behaviour after abrasion has been developed and established.

• Hydrophobic performance is present in many coatings even after considerable damage to the coating is evident.

• Good retention of water repellence can be achieved after considerable abrasion.

• Silane only treatments give the lowest level of performance

• Silica-silane hybrids are comparable with the class leading commercial products
Future trends for coatings

- Reduced VOCs
- Improved shelf-life
- Reduced processing time/cost
- Reduced harmful chemicals
- Improved mechanical performance
- Improved corrosion protection
- Enhanced temperature capability
- Improved functionality
- Improved durability
Barriers to industrial adoption

- **Application**
  - Fluoropolymers can be difficult to apply

- **Abrasion resistance**
  - All current products are relatively soft

- **High anti-fouling performance**
  - All current products are broadly hydrophobic but do not provide anti-ice, or significant oleophobic characteristics on non-porous substrates

- **Cost**
  - All current products are viewed as relatively expensive
Next generation coatings

- Closer integration of hydrophobic agent and film-forming matrix
- Use of hydrocarbons rather than fluorinated products
- Improved abrasion resistance by increasing cross-link density/inorganic content
- Low or zero solvent content
- Dual/multifunctional roughness to increase contact angle and allow coatings with anti-icing or oleophobic properties
Superhydrophobic surfaces

Image courtesy of Lotus Leaf Coatings
Wetting states – the effect of roughness

(a) Wenzel, (b) Cassie-Baxter and (c) combined model

N. Kiyassov. “High performance low energy coatings” MPhil Dissertation Cambridge University, 2009
Designing new materials

- Properties
- Structure
- Composition

Future

Vitolane® Silsesquioxanes

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Conclusions

• There are a range of low energy coatings available
• Selection depends both on functional performance and availability of cost effective solutions
• Replacement of conventional fluorinated and silicone technologies has been slow, this may be due to:
  – Performance/expectation mismatch
  – Cost
  – Availability
  – Solvent content
• Legislation is driving further development
  – Removal of fluorine
  – Increasing costs of inefficient operation
Thank you!

Any questions?

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