Advanced Low Energy Coatings

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TWI

TWI Technology Engineering

TWI Webinar

17th May 2012

Scope

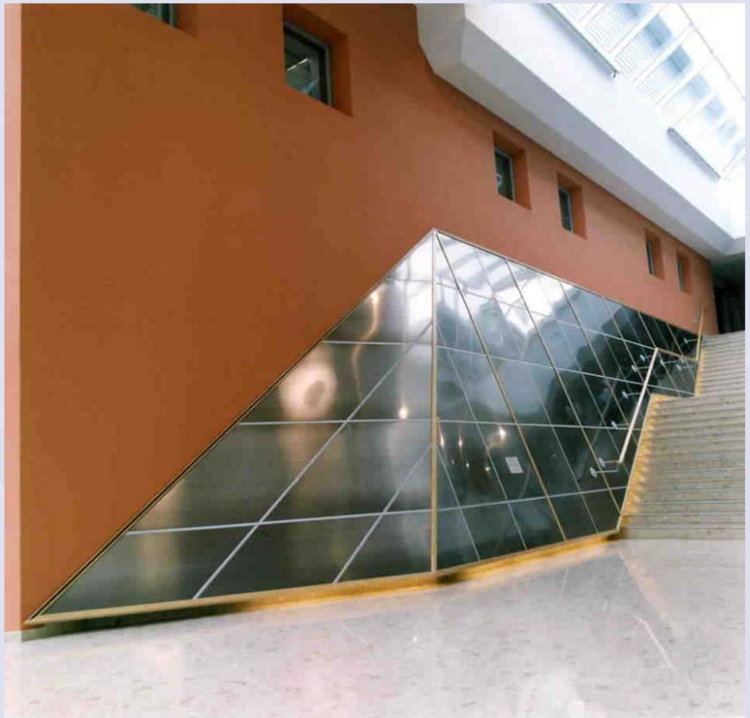
- TWI
- Industrial context
- Background to surface energy
- Commercial low energy coating market
- Comparison of selected current products
- Next generation low energy coatings
- Conclusions

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

Examples (3)

Oil & gas

Graffiti

Examples (4)


Power distribution lines

Industrial context

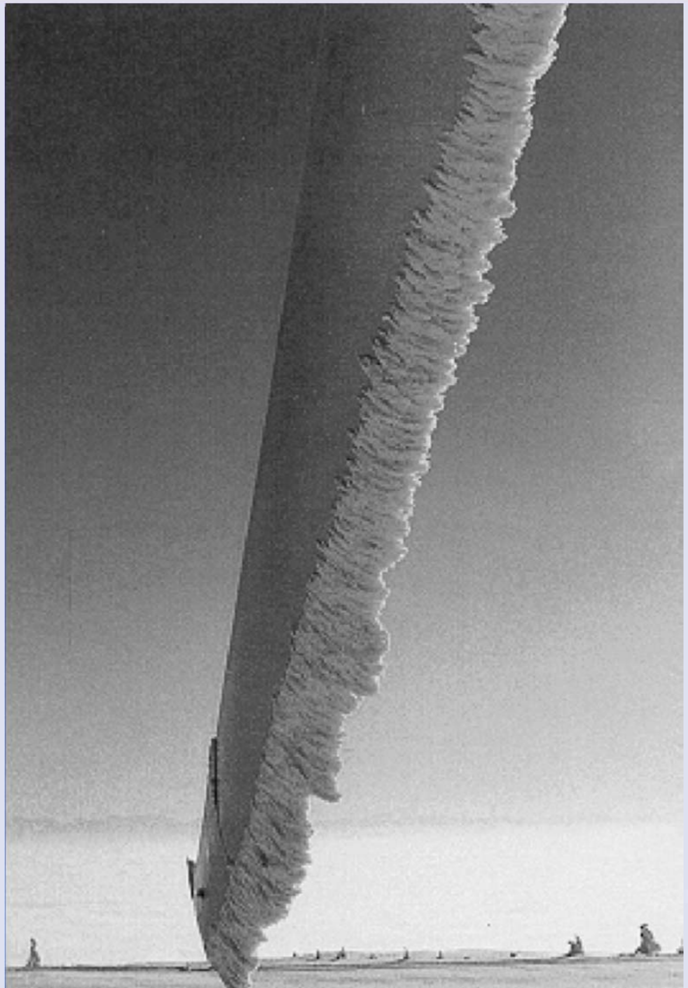
- **Fouling of surfaces**
  - increases weight
  - causes drag
  - reduces flow
  - contaminates
  - provides sites for corrosion
  - reduces efficiency
  - increases emissions
  - demands cleaning
  - increases maintenance penalty

……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**

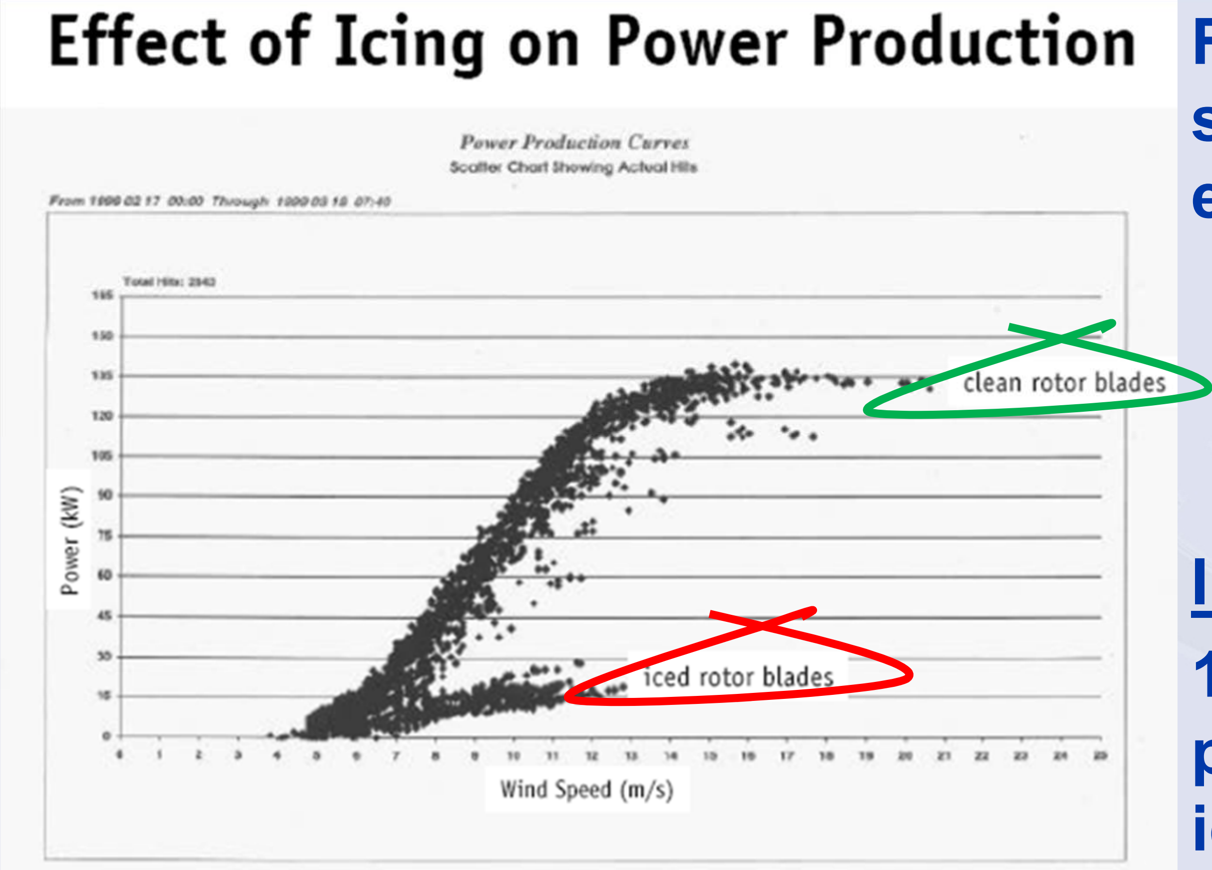
Case Study: Wind Turbines



Dalili etal. Renewable and Sustainable Energy Reviews 3 (2009) 428-438

- **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

Power: Wind Turbines



Fouling can cause significant loss of efficiency

- 25% reduction in power generation
- Icing
- Insect debris

<u>**In Yukon (on-shore)**</u>

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**

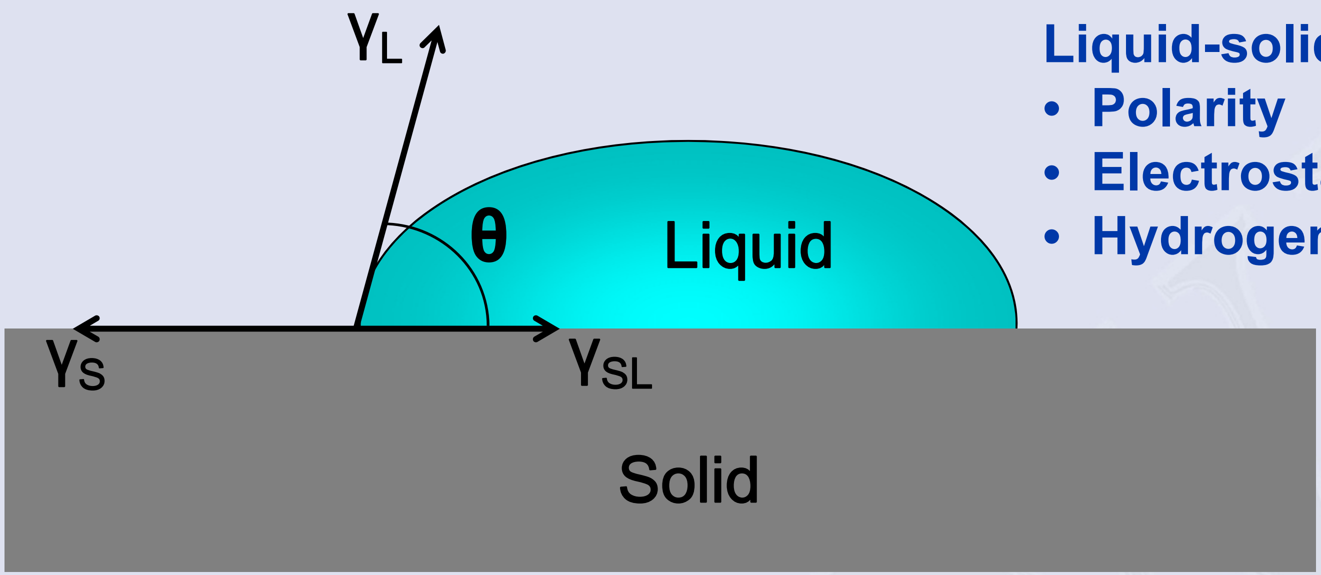
Background to surface energy

- 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



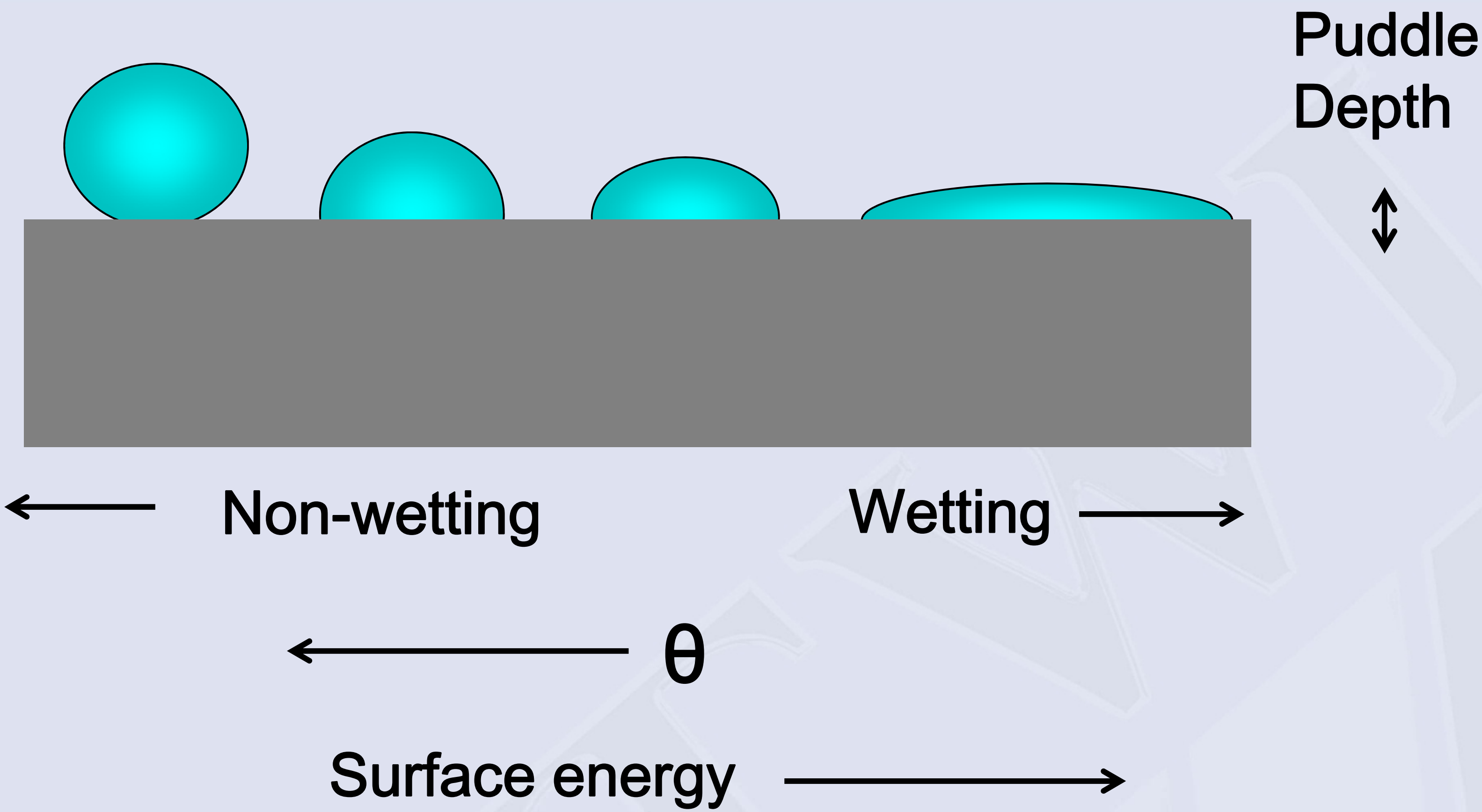
Liquid-solid interactions
- **Polarity**
- **Electrostatic forces**
- **Hydrogen bonding**

$\gamma_S = \gamma_L \cdot \cos\theta + \gamma_{SL}$ **Young Equation**

$\cos\theta_w = r\cos\theta_c$ **Wenzel Equation**

Contact angle is used as the primary measure of performance

Wetting behaviour



Definitions

- **Superhydrophilic θ < 35°**

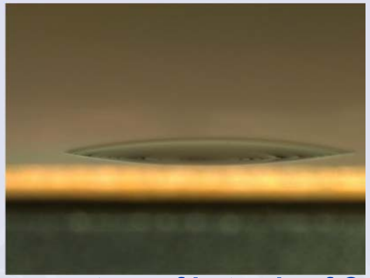


Image courtesy of Lotus Leaf Coatings

- **Hydrophobic θ > 90°**

- **Superhydrophobic θ > 150°**

Image courtesy of Lotus Leaf Coatings

Chemical considerations

Substrate	γ_c (mN/m)	WCA
Heptafluorodecyltrichlorosilane	12.0	120°
Poly(tetrafluoroethylene)	18.5	115°
Polypropylene	31.0	108°
Aluminium (3003 H14)	49	60°
Steel (A1008)	60	53°
Glass (dry)	78	<15°
Tin oxide	111	<5°

Commercial low energy coatings

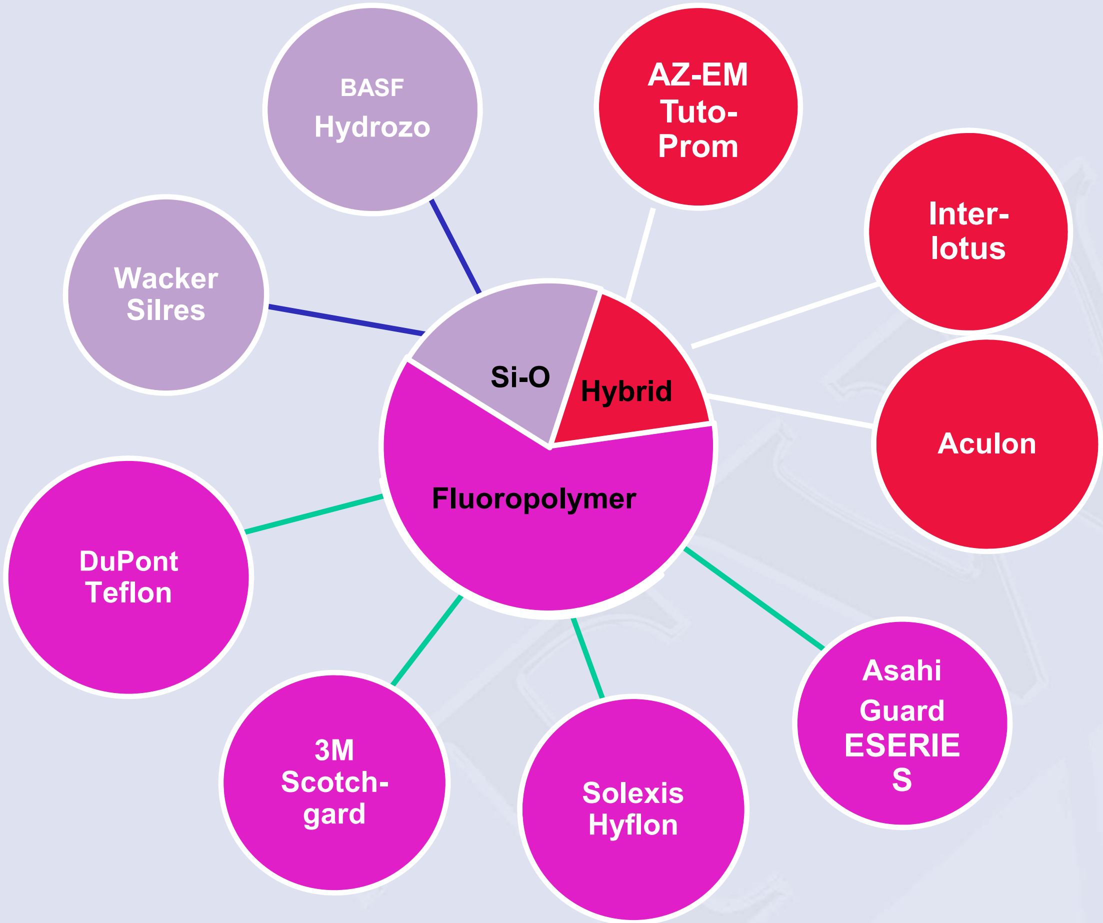
- **Market size at present $1–3Bn**

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

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

- **Future technical offerings**
  - Silazanes - Tutoprom®
  - Inorganic-organic hybrids - Interlotus

Key products and companies



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

General comparison

	Silane / Siloxane	Fluoropolymers	Hybrid
Durability	Short/medium	Medium/long	Medium/long
Chemical resistance	Good	Excellent	Excellent
Temperature resistance	Good	Excellent	Excellent
Solvent based	-	Yes	-
Gas permeable	Yes	No	Yes
Application considerations	Simple	Difficult	Simple
Cost	Med/high	High	Med/high

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
  - <u>Or</u> 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

Product/ Description	Teflon	Intersleek	Silres	TutoProm	Silicone Hardcoats
Produced by	DuPont	AkzoNobel Corporate	Wacker Silicones	Clariant / AZ-EM	Momentive Performance Materials
Industries	Healthcare, Electronics, Information, Defence Aerospace	Transport, Marine, Construction.	Construction Automobile, Aerospace, Oil & Gas, Industrial.	Railway Sanitary appliances Windshields.	Electronics, Transport, Construction Optics, Credit cards.
Company Sizes (2009)	€21,167m	€13,893m	€3,719m	€4,930m	€1,689m
Chemical Family	Fluorinated polymers	Fluorinated polymers	Silicones	Silizanes	Silicones

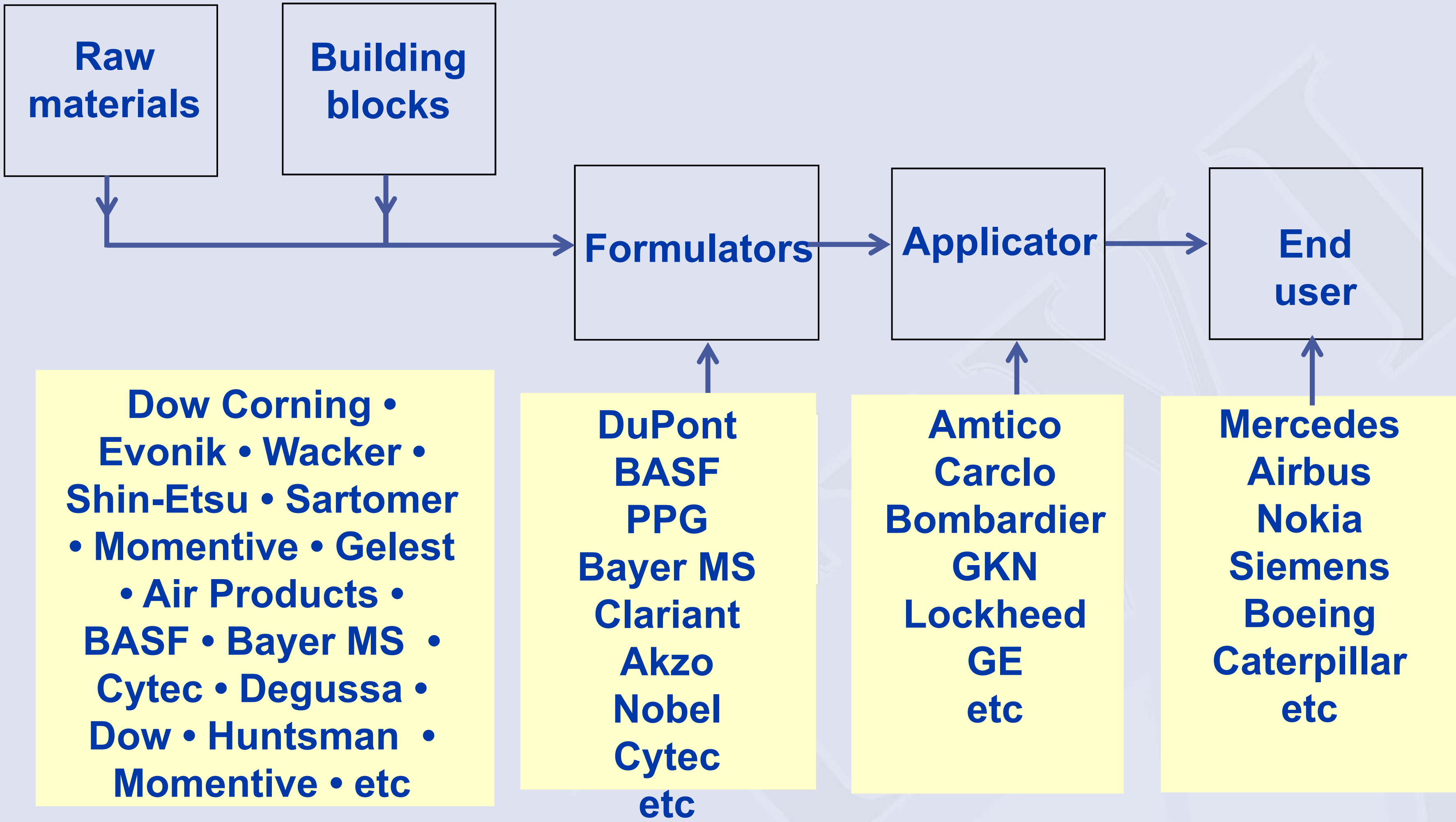
Product comparison

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

Comparative analysis (SWOT)

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

Supply Chain



Market

Market Participants In Supply Chain

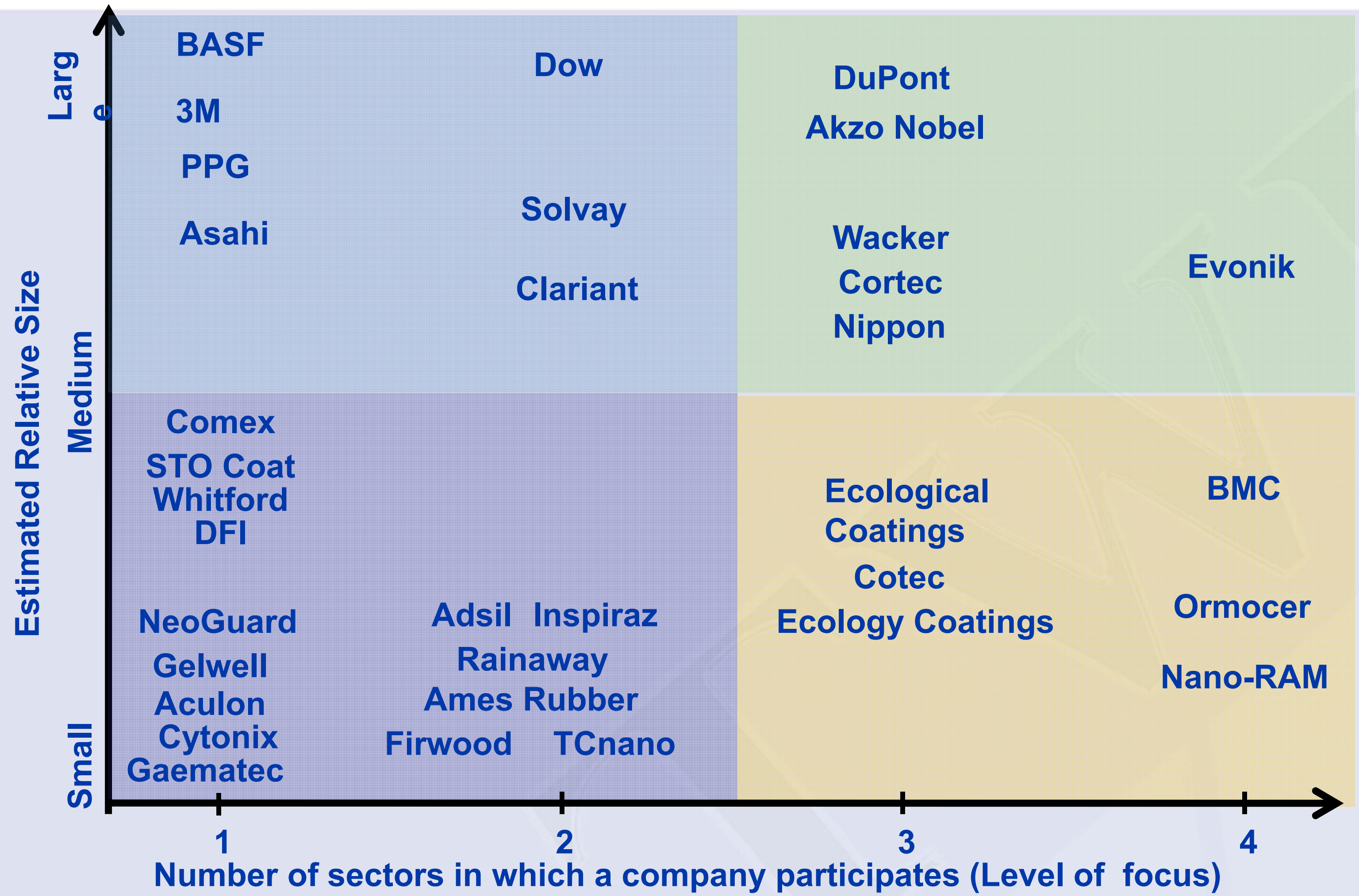
Additives
- Raw Materials & Building blocks: Evonik, Wacker,BASF, Momentive

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

Applicators
- Sinclair Optics, GKN

End Users
- GE, Lockheed

Low surface energy coating manufacturers



Case study 2: Fluoropolymer company

Strengths

- Dominant technology
- Diverse product range
- Teflon brand recognition
- Well-established supply chain

Opportunities

- Asia Pacific & Eastern Europe
- Environmentally friendly

Weaknesses

- Focused on fluoropolymers
- PFOA/PFOS hazards

Threats

- New, high-tech coating companies (disruptive innovations)
- Durability

Case study 3: Hybrid coating company

Strengths

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

Opportunities

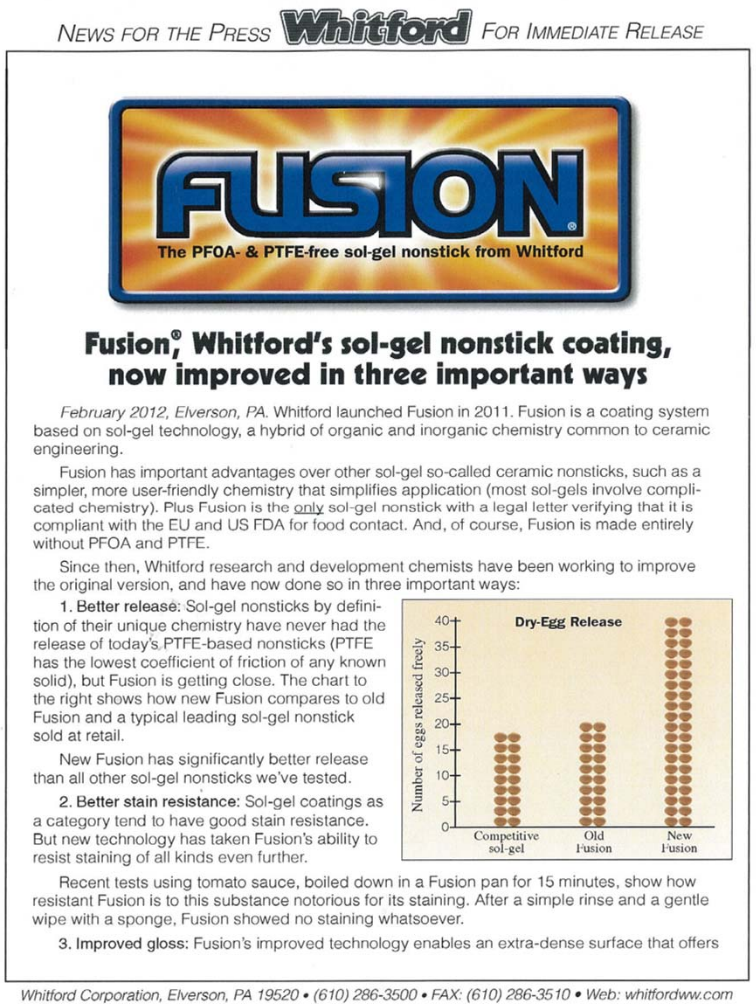
- Anti-Graffiti → Niche market
- Emerging polysilazanes (est. $93m USD)

Weaknesses

- Complex manufacturing process
- Single technology focus

Threats

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



NEWS FOR THE PRESS **Whitford** FOR IMMEDIATE RELEASE

FUSION®

The PFOA- & PTFE-free sol-gel nonstick from Whitford

Fusion®, Whitford's sol-gel nonstick coating, now improved in three important ways

February 2012, Elverson, PA. Whitford launched Fusion in 2011. Fusion is a coating system based on sol-gel technology, a hybrid of organic and inorganic chemistry common to ceramic engineering.

Fusion has important advantages over other sol-gel so-called ceramic nonsticks, such as a simpler, more user-friendly chemistry that simplifies application (most sol-gels involve complicated chemistry). Plus Fusion is the only sol-gel nonstick with a legal letter verifying that it is compliant with the EU and US FDA for food contact. And, of course, Fusion is made entirely without PFOA and PTFE.

Since then, Whitford research and development chemists have been working to improve the original version, and have now done so in three important ways:

1. **Better release:** Sol-gel nonsticks by definition of their unique chemistry have never had the release of today's PTFE-based nonsticks (PTFE has the lowest coefficient of friction of any known solid), but Fusion is getting close. The chart to the right shows how new Fusion compares to old Fusion and a typical leading sol-gel nonstick sold at retail.

New Fusion has significantly better release than all other sol-gel nonsticks we've tested.

2. **Better stain resistance:** Sol-gel coatings as a category tend to have good stain resistance. But new technology has taken Fusion's ability to resist staining of all kinds even further.

Recent tests using tomato sauce, boiled down in a Fusion pan for 15 minutes, show how resistant Fusion is to this substance notorious for its staining. After a simple rinse and a gentle wipe with a sponge, Fusion showed no staining whatsoever.

3. **Improved gloss:** Fusion's improved technology enables an extra-dense surface that offers

Whitford Corporation, Elverson, PA 19520 • (610) 286-3500 • FAX: (610) 286-3510 • Web: whitfordww.com

Mid sized fluoropolymer coating company

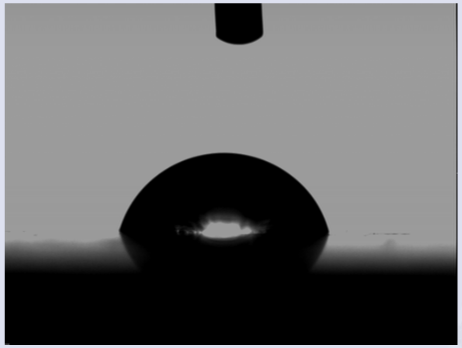
- **PFOA and PTFE free**
- **Sol-gel based**
- **Consumer product**
- **Marks the transition to new synthesis technologies**

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

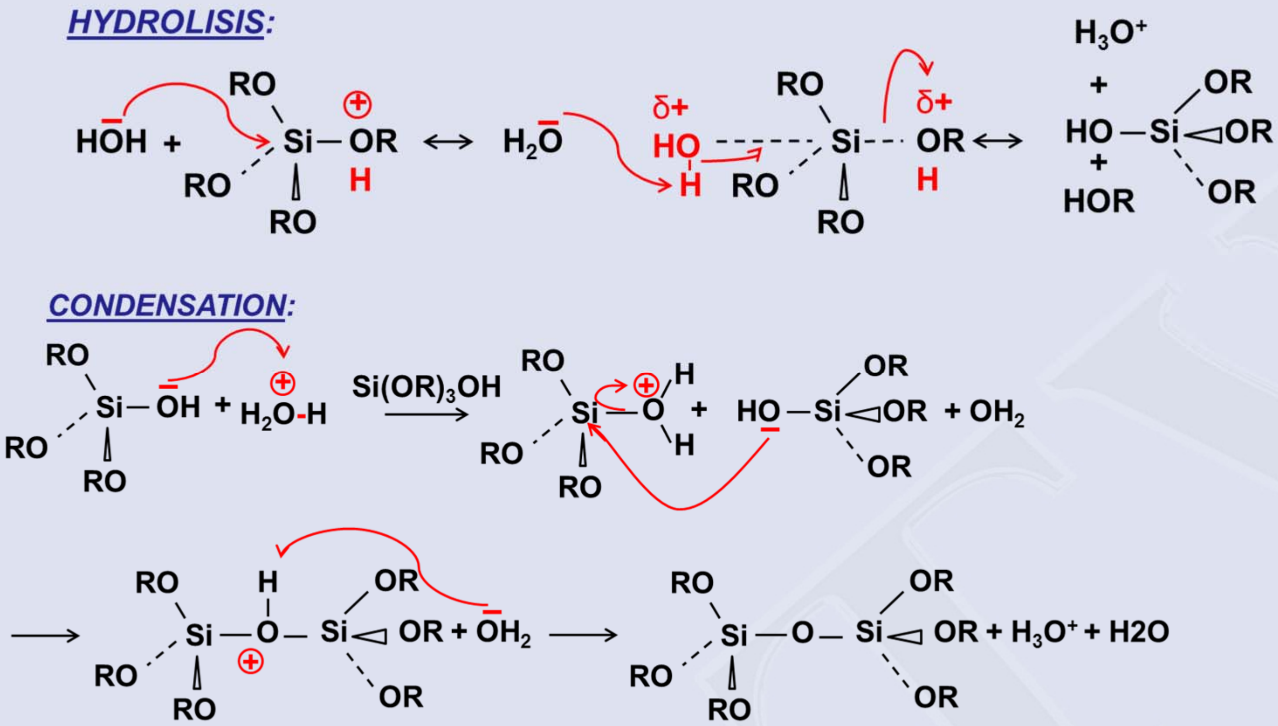
Comparison of inorganic-organic hybrids

- **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°**

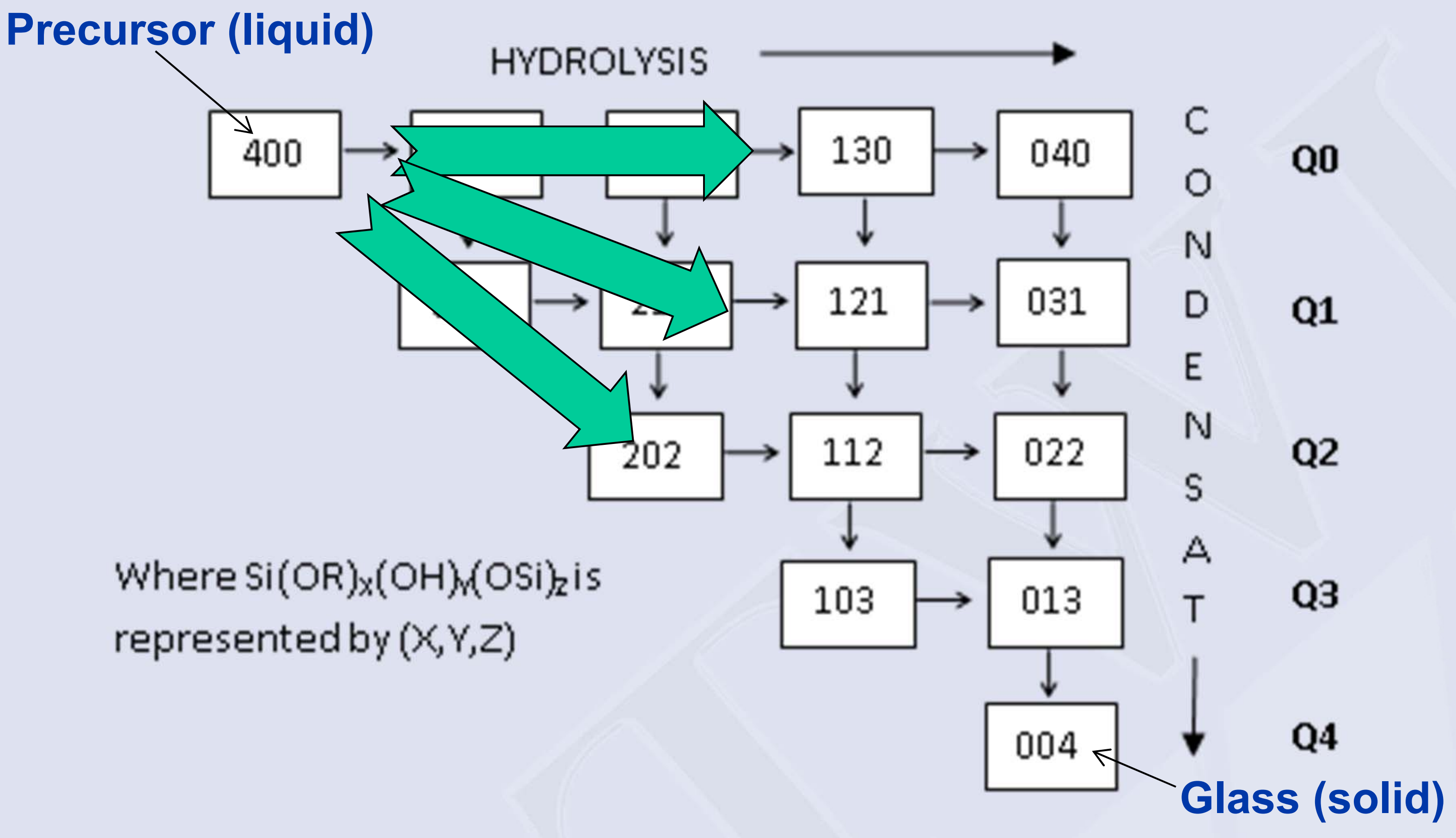


Background chemistry

Silica network formation via sol-gel reactions



Sol-gel: Structural evolution

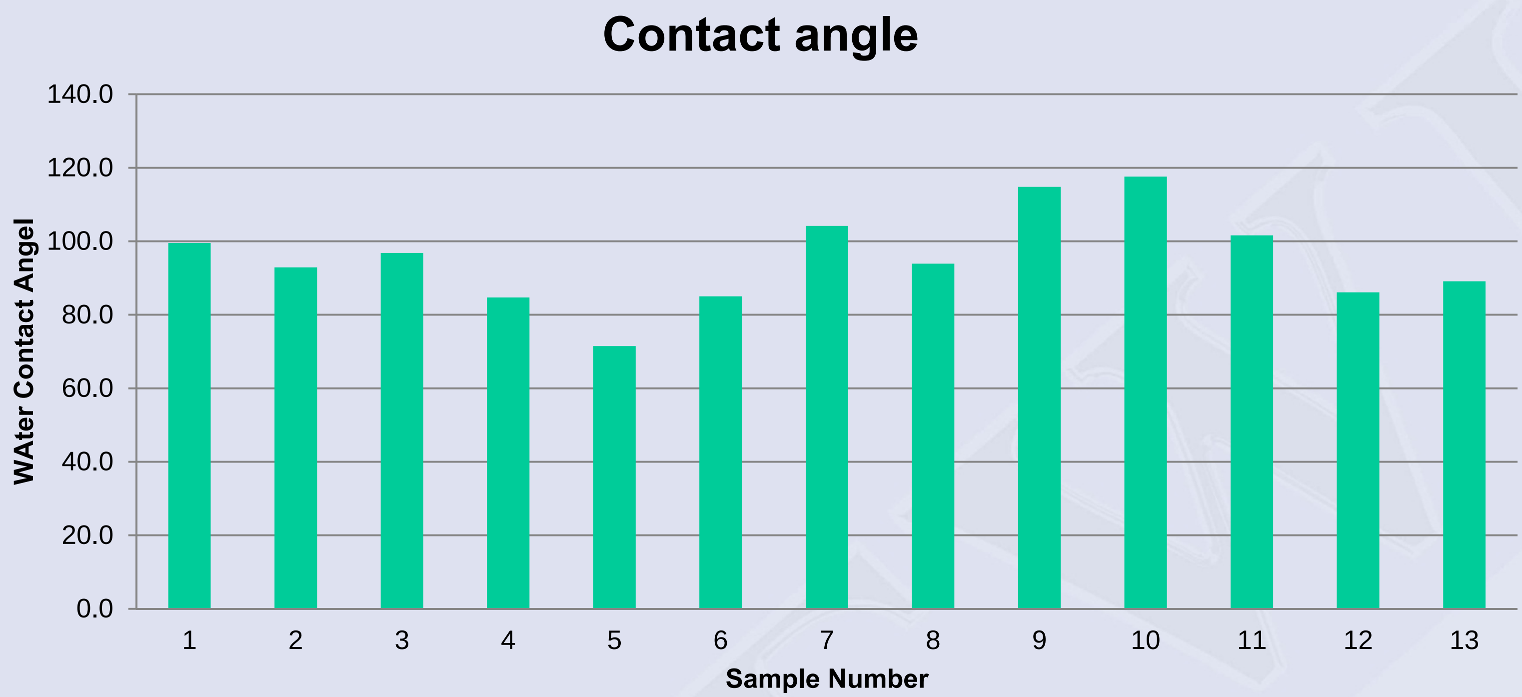


Matrix representation of the chemical evolution of a sol-gel system (Assink and Kay, 1984).

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

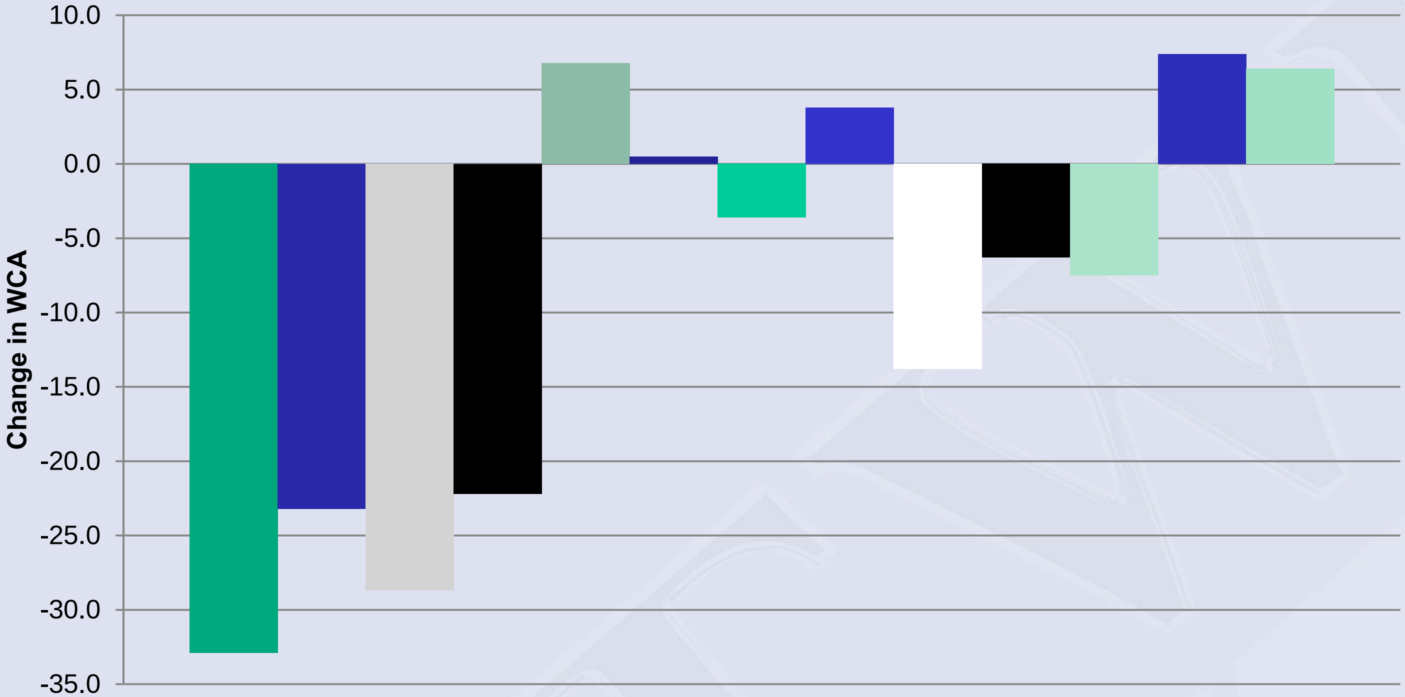
Comparison of aluminium coated samples



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 lint free cloth - aluminium substrate



Samples 1-4 Monolayer silanes
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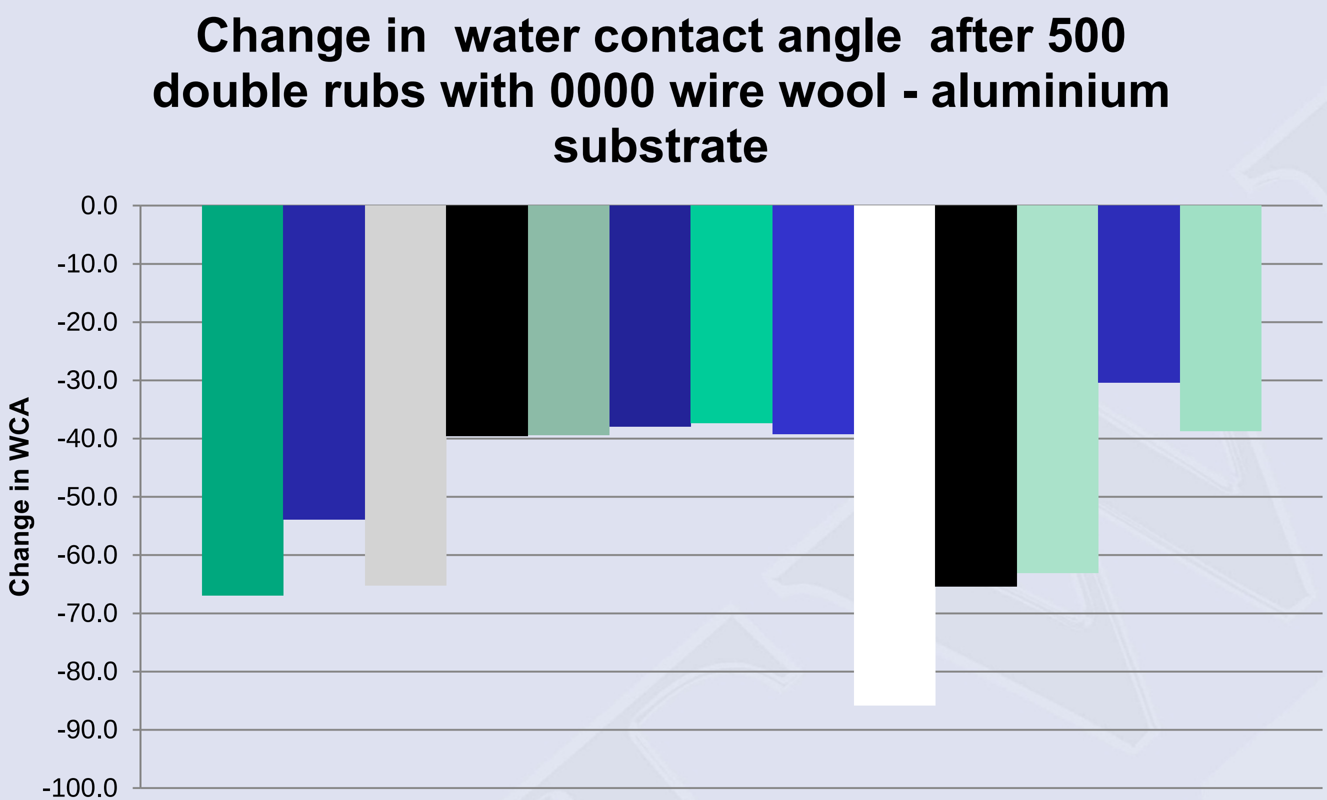
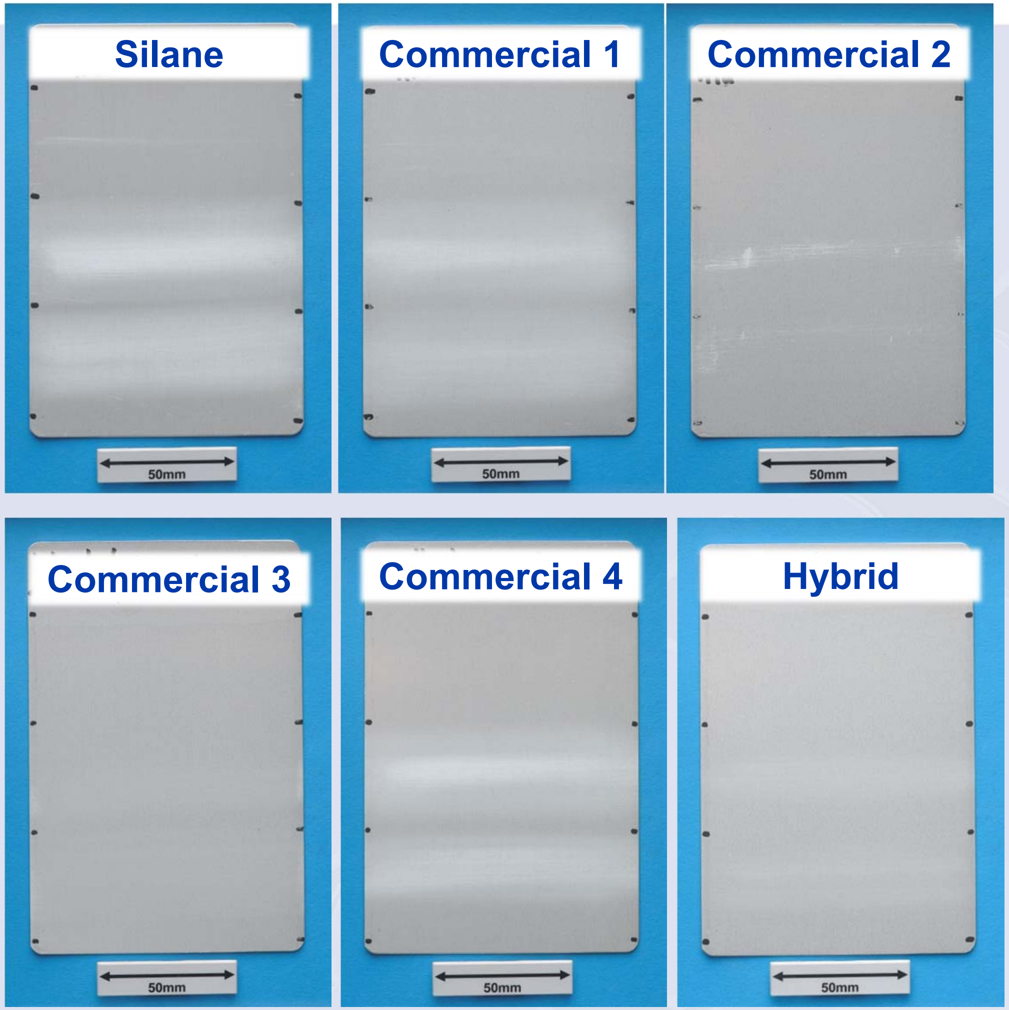
Comparison

Abrasion resistance on aluminium



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

Wear damage after 10 double rubs



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**

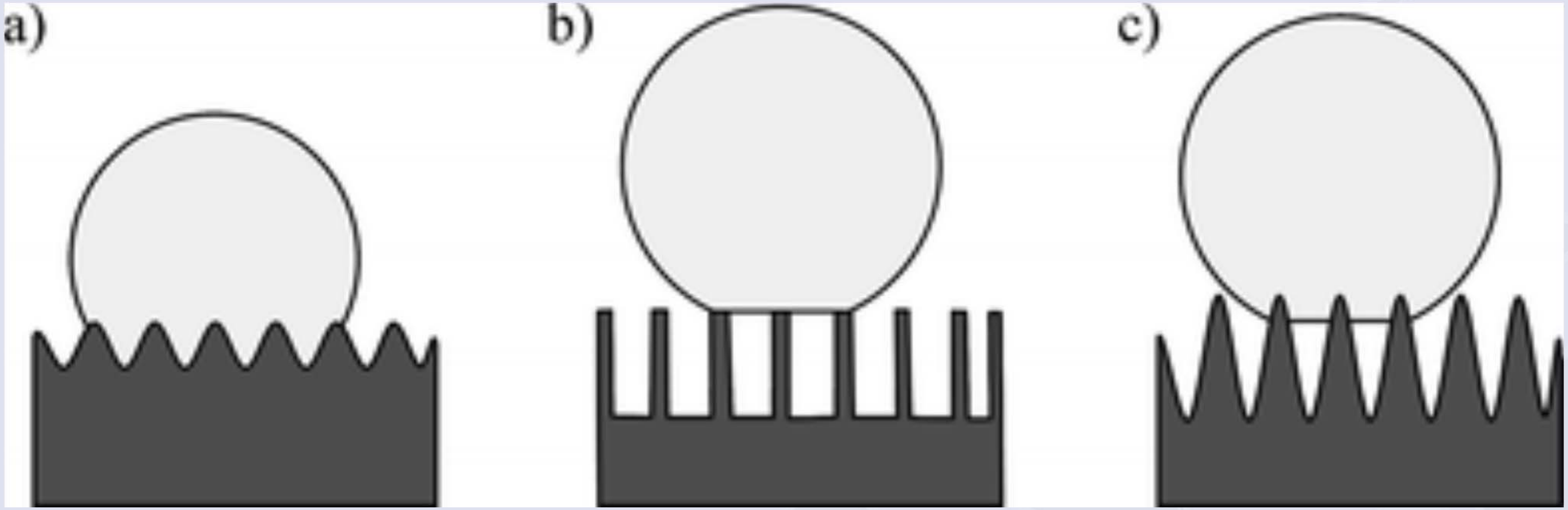
Next generation coatings

- Closer integration of hydrophobic agent and film-forming matrix
- Use of hydrocarbons rather that 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

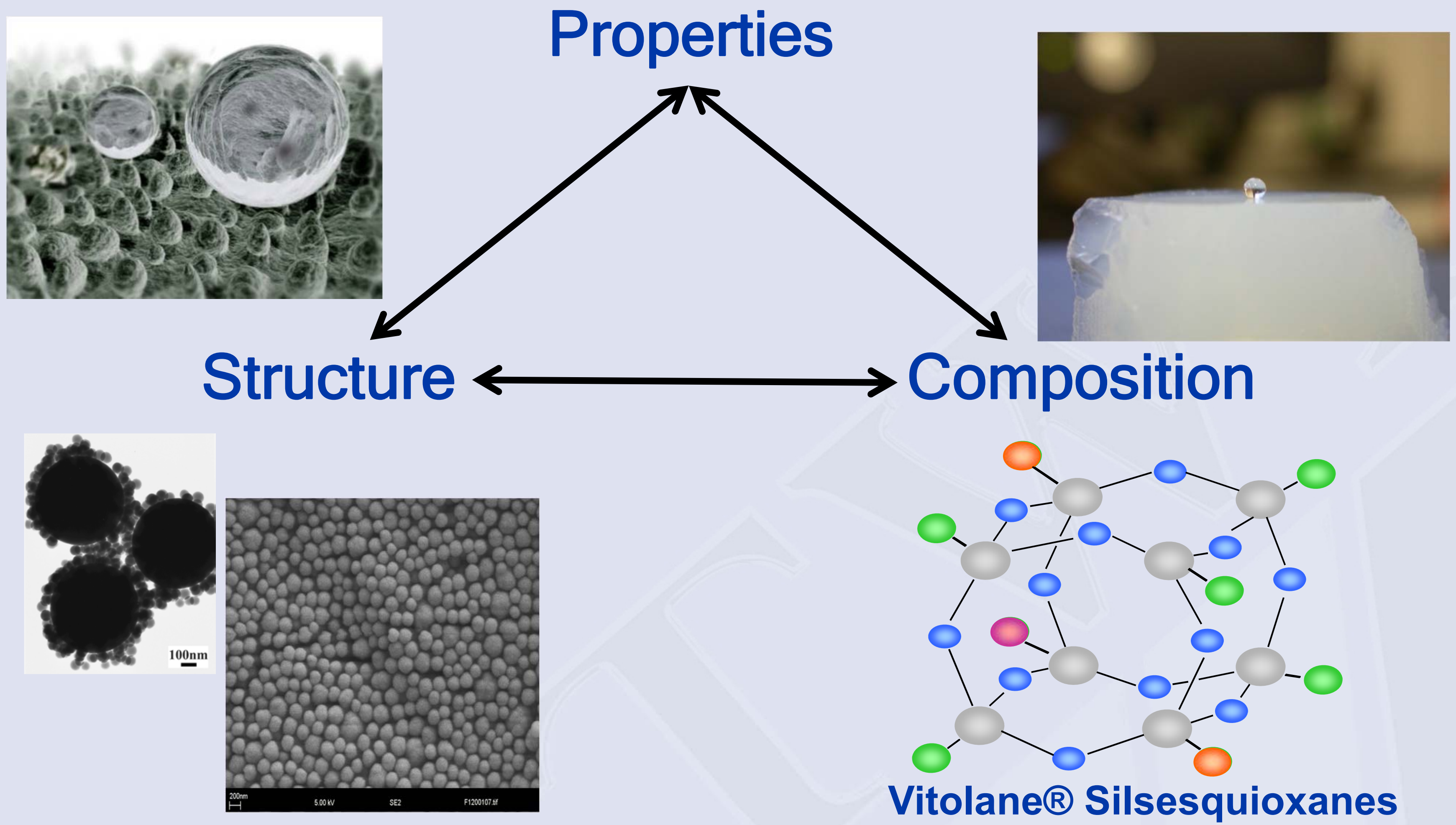
Wetting states – the effect of roughness



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

N. Kiyassov. "High performance low energy coatings" MPhil Dissertion Cambridge University, 2009

Designing new materials



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Future

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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