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Novel Methodology for the Highly-Efficient Separation of Oil and Water

16 March 2014

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Non-wetting surfaces

Contact angles with water:

- **Superhydrophilic**: $\theta \sim 0^\circ$
- **Hydrophilic**: $0^\circ < \theta < 90^\circ$
- **Hydrophobic**: $\theta > 90^\circ$
- **Superhydrophobic**: $\theta^* > 150^\circ$

Similarly, superoleophobic surfaces display contact angle $\theta^* > 150^\circ$ with oils or alkanes.
Nanocomposite Materials

POSS

Nanosilicas

Layered silicates

Linear silicates

Water
Methylene Iodide
Octane
Methanol

\[ \gamma_v = 22.7 \, \text{mN/m} \]
\[ \gamma_v = 27.5 \, \text{mN/m} \]
\[ \gamma_v = 50.8 \, \text{mN/m} \]
\[ \gamma_v = 72 \, \text{mN/m} \]
Fluorinated POSS Synthesis

\[ R_f \text{Si}X_3 + \text{OH}^-/\text{H}_2\text{O} \rightarrow R_f \text{SiX}_3 \]

\[ R_f = -\text{CH}_2\text{CH}_2(\text{CF}_2)_n\text{CF}_3 \]

\[ n = 0, 3, 5, 7 \]

Angew Chem 2008

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Hydrophobic Materials

- Spin-cast surface of Fluorodecyl POSS
- $\sim 4 \, \mu m$ rms roughness by AFM
- $154^\circ$ Water contact angle

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Zisman Analysis

Fluorodecyl:
\[ R = -\text{CH}_2\text{-CH}_2\text{-}(\text{CF}_2)_7\text{-CF}_3 \]

GG analysis results in surface energy calculation of: \( \gamma_c = 8 \text{ mN/m} \)

Contacting liquids:
- hexadecane (\( \gamma_{lv} = 27.5 \text{ mN/m} \)), dodecane (25.3), decane (23.8),
- octane (21.6), heptane (20.1) and pentane (15.5)
The Lotus Leaf

Water, $\gamma_{LV} = 72.1 \text{ mN/m}$

Hexadecane, $\gamma_{LV} = 27.5 \text{ mN/m}$

On most surfaces, $\theta_{oil} < \theta_{water}$. This is because the surface tension ($\gamma_{LV}$) of water is significantly higher than that for oils.
Critical role of re-entrant texture ($\psi < 90^\circ$)

$\theta < 90^\circ$ ; $\psi < 90^\circ$

It is possible to support a composite interface even if $\theta < 90^\circ$

Re-entrant curvature : $180^\circ > \theta > 0^\circ$

Lotus Leaf

Cylinders / Fibers

• Constructing super-repellent surfaces
  – Three key ingredients

Surface Chemistry ($\theta_e$)

Roughness ($r$)

Surface Geometry ($\psi$)

PMMA + 44 wt% POSS electrospun coating (beads on a string) morphology
The Dip-Coating Process

Before dip-coating with a solution of fluorodecyl POSS

**Dip**

Solution of fluorodecyl POSS in Asahiklin (30 mg/ml)

**Dry** (heat in oven at 60°C for 20 minutes)

Hexadecane ($\gamma_{lv} = 27.5$ mN/m) on an as-received commercial polyester fabric

After dip-coating with a solution of fluorodecyl POSS
Dip-Coated Polyester Fabric

Before coating

After coating with fluorodecyl POSS in Asahiklin (30 mg/ml)

Hexadecane

\[ \gamma_v = 22.7 \text{ mN/m} \]
\[ \gamma_v = 27.5 \text{ mN/m} \]
\[ \gamma_v = 50.8 \text{ mN/m} \]
\[ \gamma_v = 72 \text{ mN/m} \]

Methanol  Hexadecane  Methylene Iodide  Water
Dip-coating process for conformal coating of textured surfaces

**Rf = -CH$_2$-CH$_2$-(CF$_2$)$_7$-CF$_3$**
Fluorodecyl POSS

$\gamma_{sv} \approx 8 \text{ mN/m}$

**Tecnoflon° (BR9151)**
Fluoro-elastomer from Solvay-Solexis

$\gamma_{sv} \approx 18 \text{ mN/m}$

50:50 mixture, total solids = 10 mg/ml

- Dip in Asahiklin solution for 5 minutes
- Air dry to remove solvent
- Heat treat at 60 °C for 30 minutes

**Anticon 100 polyester fabric**

**EDAXS spectrum for fluorine**
At low POSS concentrations many surfaces are both superhydrophobic and superoleophilic ($\theta^*_{\text{alkane}} \approx 0^\circ$). Thus, these porous surfaces form ideal membranes for separating mixtures / dispersions of alkanes (oils) and water.


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PEGDA + Fluorodecyl POSS

Can hydrogen bond with water

AFM Phase images of spin-coated PEGDA + POSS films

Photo-crosslinkable

Fluorodecyl POSS molecules preferentially segregate to the air interface and crystallize.

Fluorodecyl POSS

$R_f = -\text{CH}_2\text{-CH}_2\text{-} (\text{CF}_2)_7\text{-CF}_3$

$\gamma_{sv} \approx 8 \text{ mN/m}$
PEGDA + Fluorodecyl POSS
PEGDA + fluorodecyl POSS blends

Surfaces with inherent re-entrant curvature dip-coated with PEGDA + POSS blends

Stainless Steel Wire Mesh

Commercial Polyester Fabric

PEGDA surface reconfiguration leads to superhydrophilic behavior.
Free oil – water separation

Stainless steel mesh coated with PEGDA + 20 wt% fluorodecyl POSS.
Free oil – water separation
1-Liter scale separation
Separation of Oil-Water Emulsions

Water-in-Oil Emulsion

Composition: 93% Oil, 7% Water

Oil-in-Water Emulsion

Composition: 76% Oil, 24% Water

A simple, scalable, gravity-based system for the separation of both oil-in-water and water-in-oil emulsions. This is one of the first gravity-based systems to achieve such high emulsion separation efficiencies.
Gravity-driven, continuous-flow device
Oil-Water Emulsion Separation

Our system: PEGDA + 20% FPOSS

Flux (L/hr·m²)

Cycles
Separation Efficiency

Time (min)

Weight %

Feed
Permeate
Retentate

99% Oil
78% Oil
0.1% Oil

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Summary

• We have developed surfaces that for the first time are superhydrophilic and superoleophobic.

• Such surfaces are ideal for the separation of both free-oil and oil-water emulsions.

• The designed membranes, for the first time, allow continuous-flow oil-water emulsion separation.
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Professor Anish Tuteja
Oil/Water Separation Membranes

Polymer Working Group
Fluorinated POSS

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Air Force Office of Scientific Research

Air Force Research Laboratory, Propulsion Directorate
Impact of a Novel Fuel Processing Technique

Payload:
$0.5B - 2B
10-15 yr.

Launch Vehicle:
$40M - 100M

Fuel
$100k

Price of fuel is influenced by many variables other than raw material cost

A novel fuel processing technique will enable:
Composition modification without the need of large refineries
Preparation of fuel in remote locations
Assured access
Reduced logistics costs

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Vision

To develop the capability to produce high-performance military fuels at reduced cost with increased availability.
Thesis: Use liquid/liquid extraction to provide improvements in several critical areas

Objective: Utilize liquid/liquid extraction process to improve performance, increase availability, and reduce cost of RP by producing these fuels from less expensive feed streams.

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Undesirables in RP-1

**Oil Red B4 (ORB4)**
Dye in RP-1
65 wt% Solvent Red 164

- 15-30 wt% xylene
- 5-10 wt% ethylbenzene

**Sulfur Compounds**
Present in RP-1
Concentration varies

- Mercaptans
- Sulfides
- Thiophenes

**Aromatics**
Present in RP-1
Concentration varies

Detrimental to Thermal Stability!

Catalysts for Coking Reactions

Detrimental to Performance

RP-2 is expensive and requires an additional supply chain, which also consumes resources and may be put at risk due to unforeseen circumstances.

Removal from less expensive feed streams will increase availability, reduce supply risk, reduce cost, and improve performance.
Visible spectroscopy was used to determine concentration of dye from 2-40 ppm.

Small scale extractions show IPA is the most efficient extraction solvent for dyes.

Higher IPA : Water ratio results in higher dye concentration.

Optimum IPA : Water ratio is ~13 : 1 based on small scale extractions.
Equilibrium curve for compounds extracted from dodecane with IPA:water 10:1 v:v ratio
Extraction Apparatus

IPA / Water Inlet Spray

Hydrophobic / Oleophillic Membrane (passes oil, not water)

RP Inlet Spray

Oleophobic / Hydrophillic Membrane (passes water, not oil)

RP Outlet

RP Phase

Emulsion Phase

IPA / Water Outlet

Water (IPA) Phase
**Extraction of Sulfur from RP-1**

<table>
<thead>
<tr>
<th>Sulfur Compounds by GC-SCD (Sulfur Speciation)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 Thiophenes</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>C3-C4 Thiophenes</td>
<td>1.6</td>
</tr>
<tr>
<td>C5 Thiophenes</td>
<td>6.3</td>
</tr>
<tr>
<td>C6 Thiophenes</td>
<td>6.1</td>
</tr>
<tr>
<td>C7 Thiophenes</td>
<td>5.8</td>
</tr>
<tr>
<td>C8-C9 Thiophenes</td>
<td>4.9</td>
</tr>
<tr>
<td>C10 Thiophenes</td>
<td>1.3</td>
</tr>
<tr>
<td>C11 Thiophenes</td>
<td>0.9</td>
</tr>
<tr>
<td>C12+ Thiophenes</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Sulfur Compounds by GC-SCD (Sulfur Speciation)**

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<tr>
<td>C12+ Thiophenes</td>
</tr>
</tbody>
</table>

*Standard Grade RP-1 (Errors are ±0.3 ppm)*

*Standard Grade RP-1 after extraction with 10:1 IPA water in extraction apparatus*
Applied Materials Group

The Applied Materials Group at Edwards Air Force Base

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Mr. Jacob Marcischak
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QUESTIONS?

U.S. AIR FORCE