REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
March 2014

2. REPORT TYPE
Briefing Charts

3. DATES COVERED *(From - To)*
March 2014- April 2014

4. TITLE AND SUBTITLE
Novel Methodology for the Highly-Efficient Separation of Oil and Water (Briefing Charts)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Joseph Mabry, Anish Tuteja, Andrew Guenthner, Josiah Reams, Arun Kota, Gibum Kwon, Wonjae Choi

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
Q014

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory (AFMC)
AFRL/RQRP
10 E. Saturn Blvd.
Edwards AFB CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RQ-ED-VG-2014-051

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Approved for Public Release; Distribution Unlimited.

13. SUPPLEMENTARY NOTES
Briefing charts presented at ACS National Meeting and Expo, Dallas, TX, 16 March 2014. PA#14128

14. ABSTRACT
Briefing Charts

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Joseph Mabry
Unclassified	**Unclassified**	**Unclassified**	SAR	37	**19b. TELEPHONE NO** *(include area code)* 661-275-5857

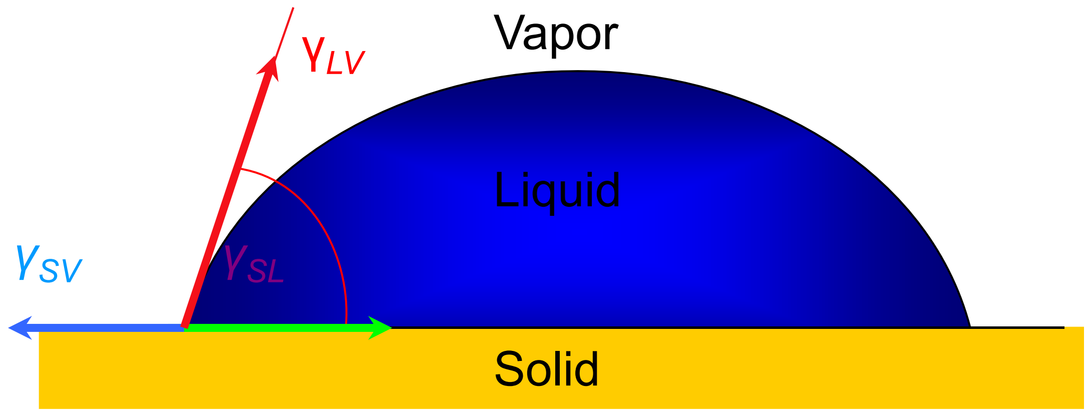
Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

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

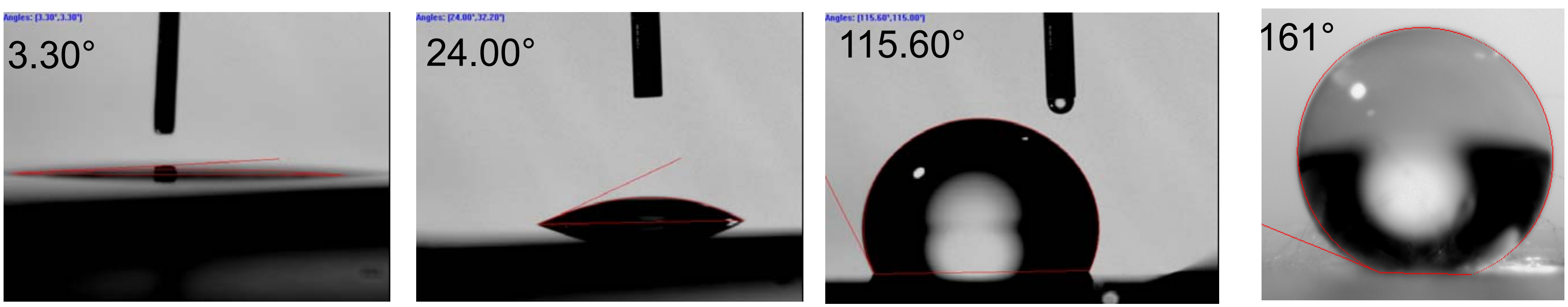
16 March 2014

Joseph Mabry, Anish Tuteja, Andrew Guenthner, Josiah Reams,
Arun Kota, Gibum Kwon, Wonjae Choi
Air Force Research Laboratory
Aerospace Systems Directorate
joseph.mabry@us.af.mil
(661) 275-5857

Non-wetting surfaces



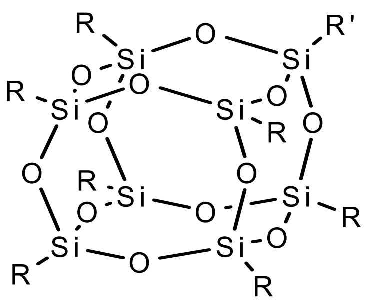
Contact angles with water:



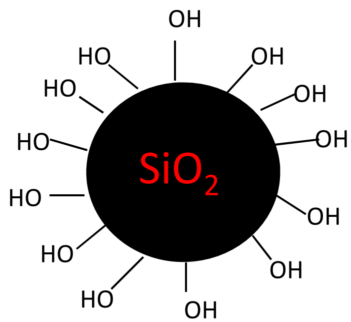
Superhydrophilic	Hydrophilic	Hydrophobic	Superhydrophobic
$\theta \sim 0°$	$0° < \theta < 90°$	$\theta > 90°$	$\theta^{*} > 150°$

Similarly, superoleophobic surfaces display contact angle $\theta^{*} > 150°$ with oils or alkanes

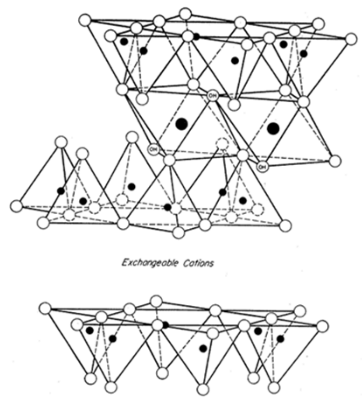
Nanocomposite Materials



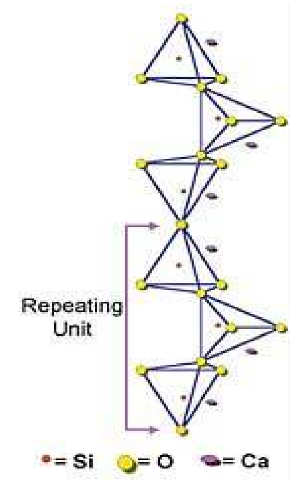
POSS



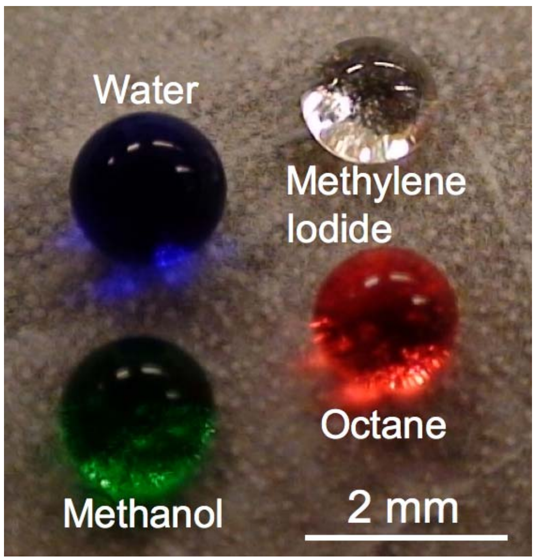
Nanosilicas

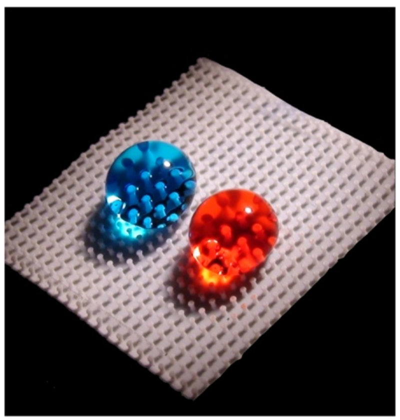


Layered silicates



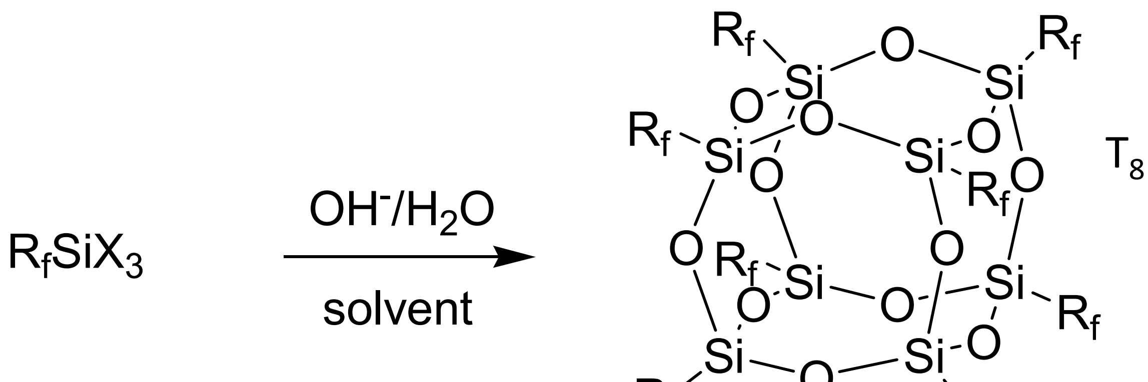
Linear silicates





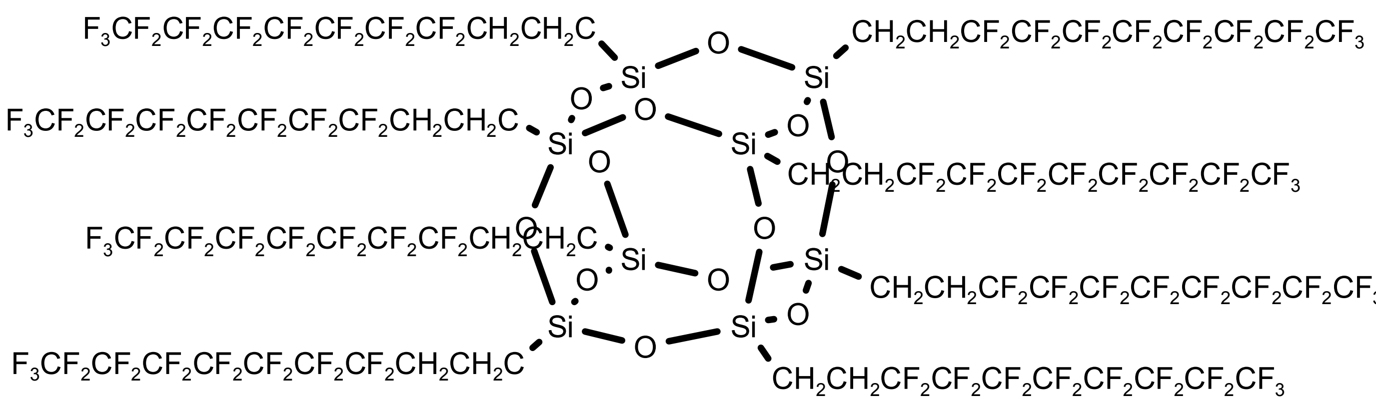
DISTRIBUTION A. Approved for public release; distribution unlimited.

Fluorinated POSS Synthesis



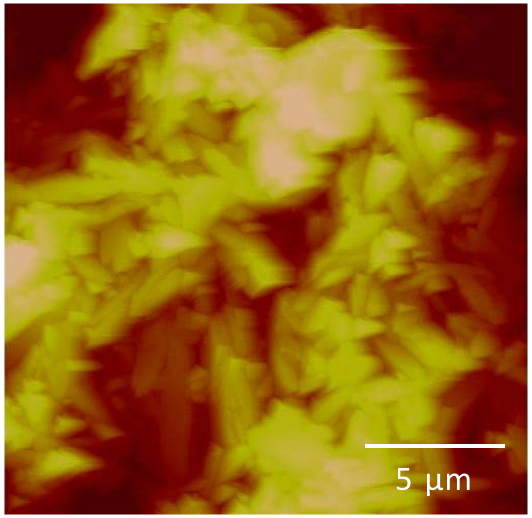
$R_f = -CH_2CH_2(CF_2)_nCF_3$

$n = 0, 3, 5, 7$

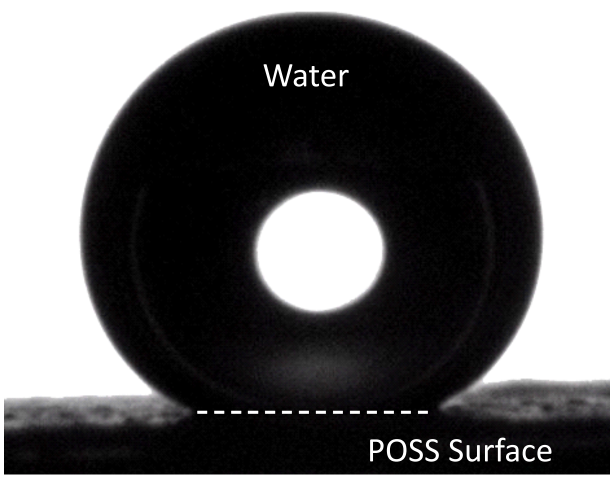


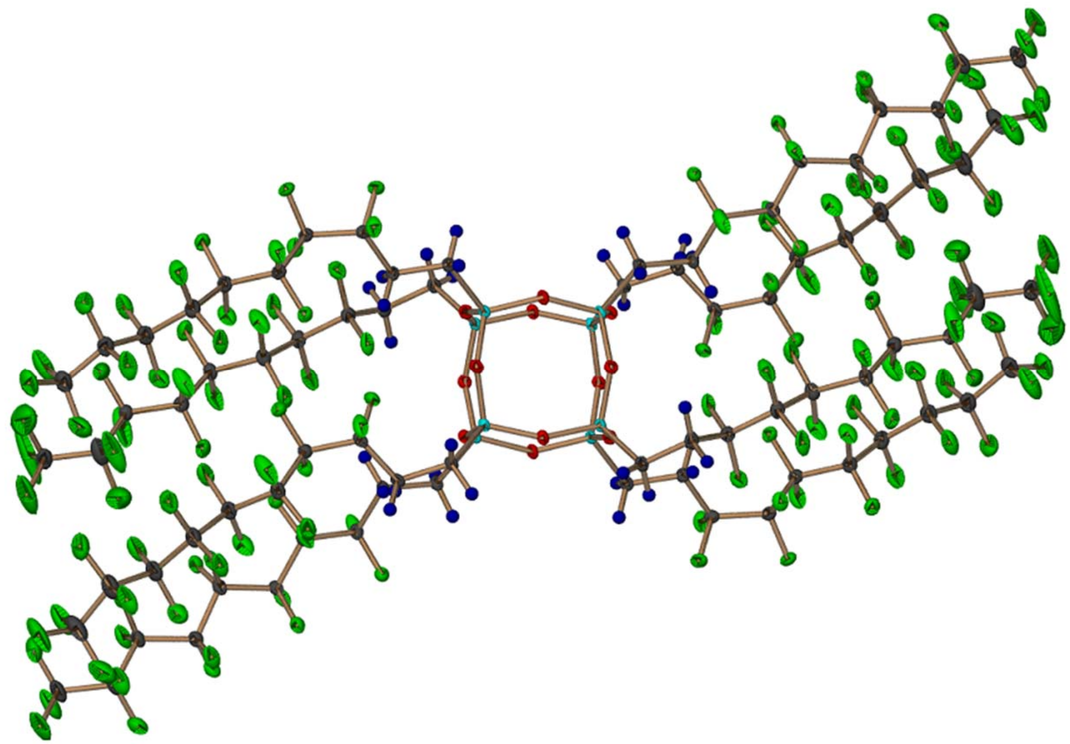
Angew Chem 2008

Hydrophobic Materials



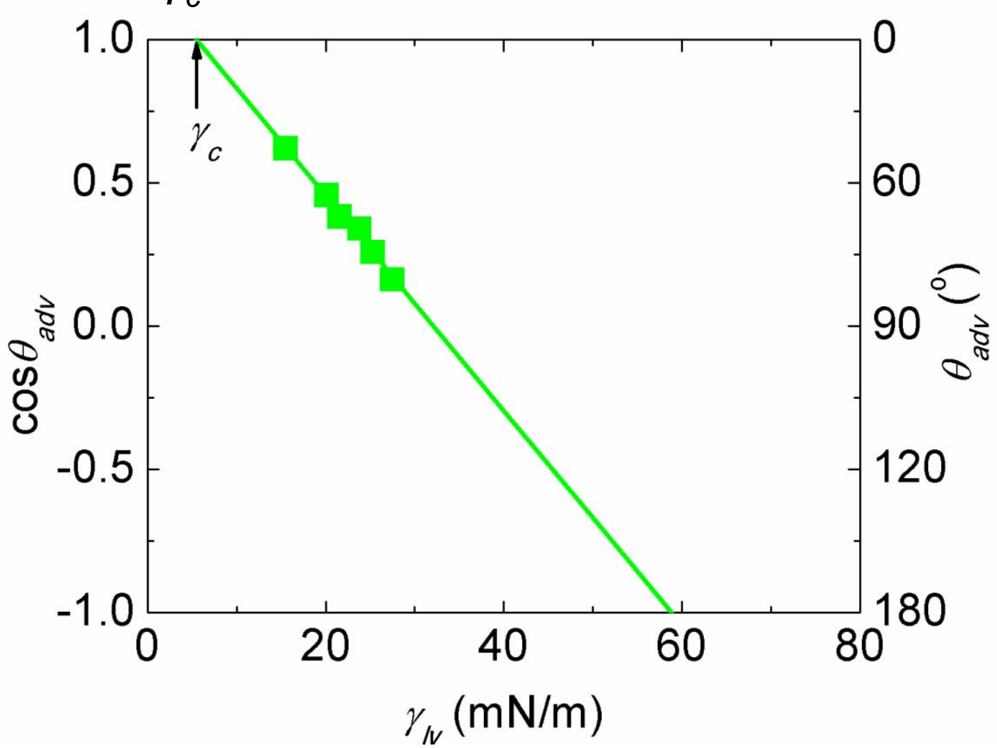
- Spin-cast surface of Fluorodecyl POSS
- ~4 μm rms roughness by AFM
- 154° Water contact angle

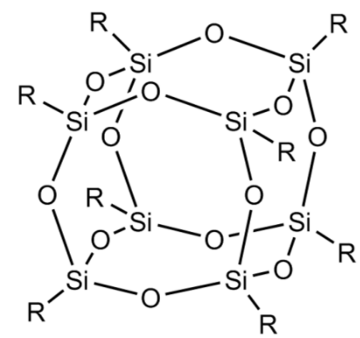




Zisman Analysis

γ_c = 5.5 mN/m



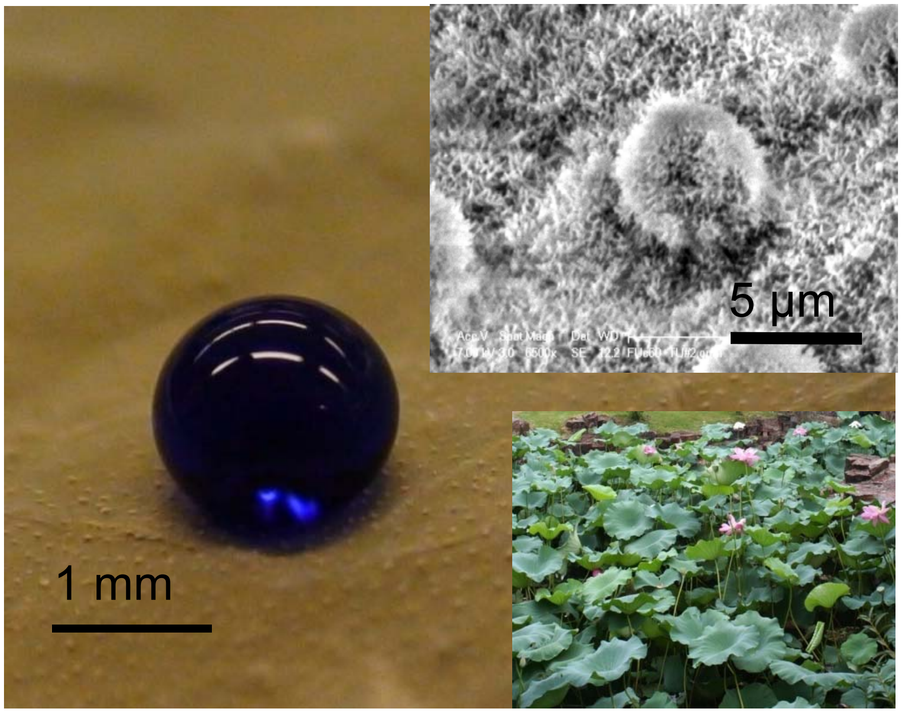


Fluorodecyl:
$R = -CH_2-CH_2-(CF_2)_7-CF_3$

GG analysis results in surface energy calculation of: γ_c = 8 mN/m

Contacting liquids:
hexadecane (γ_{lv} = 27.5 mN/m), dodecane (25.3), decane (23.8), octane (21.6), heptane (20.1) and pentane (15.5)

The Lotus Leaf

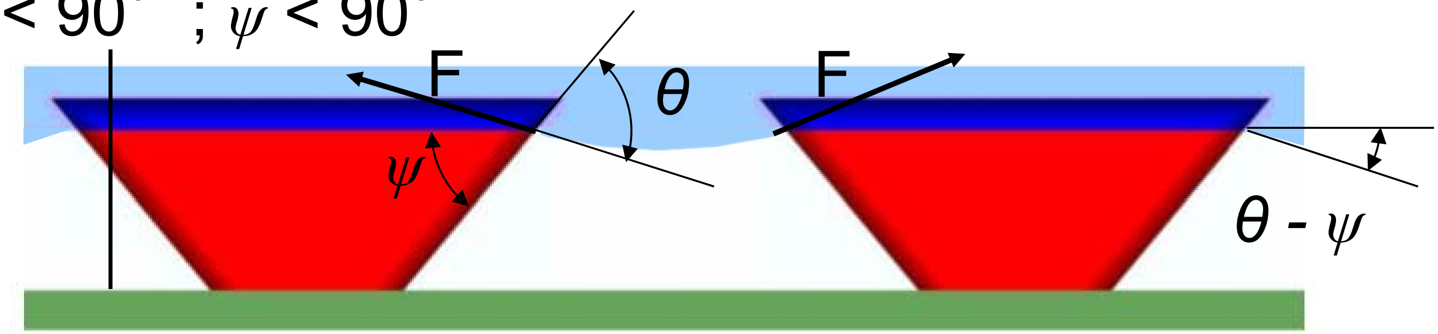


Water, γ_{LV} = 72.1 mN/m

Hexadecane, γ_{LV} = 27.5 mN/m

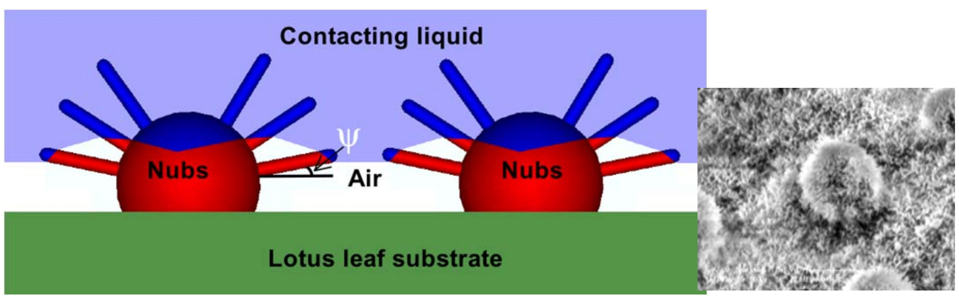
On most surfaces, $\theta_{oil} < \theta_{water}$. This is because the surface tension (γ_{lv}) of water is significantly higher than that for oils.

Critical role of re-entrant texture (ψ < 90°)

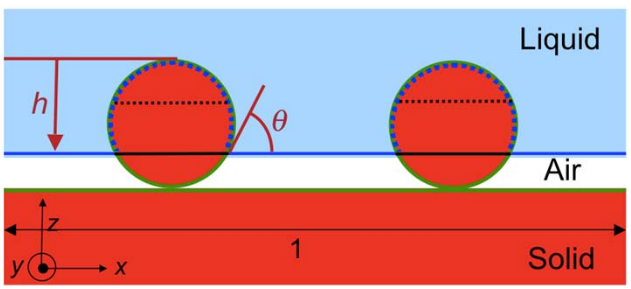


It is possible to support a composite interface even if θ < 90°

Re-entrant curvature : 180° > θ > 0°



Lotus Leaf



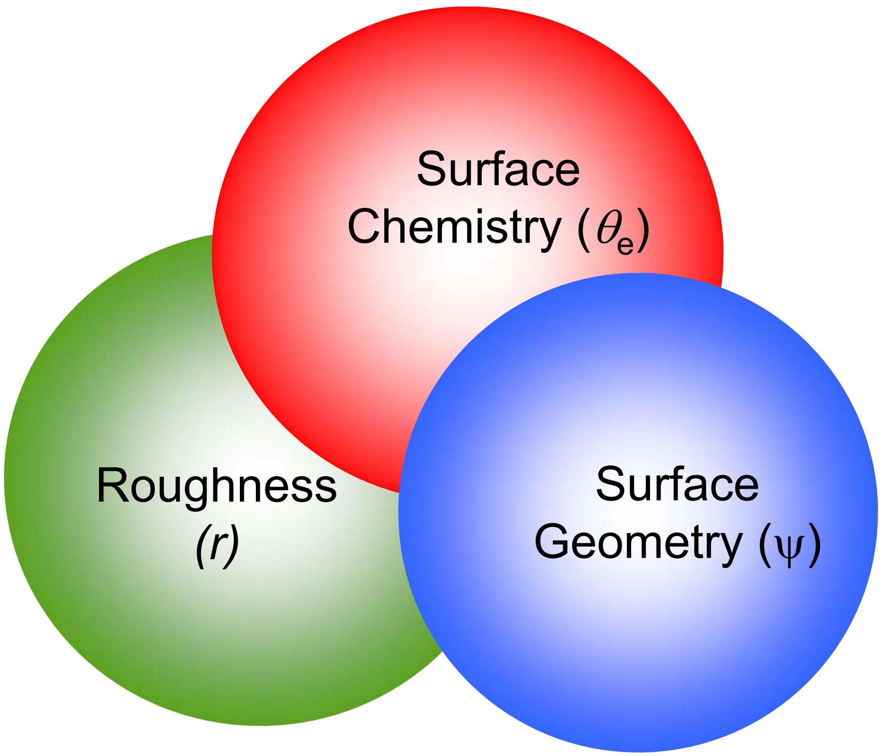
Cylinders / Fibers

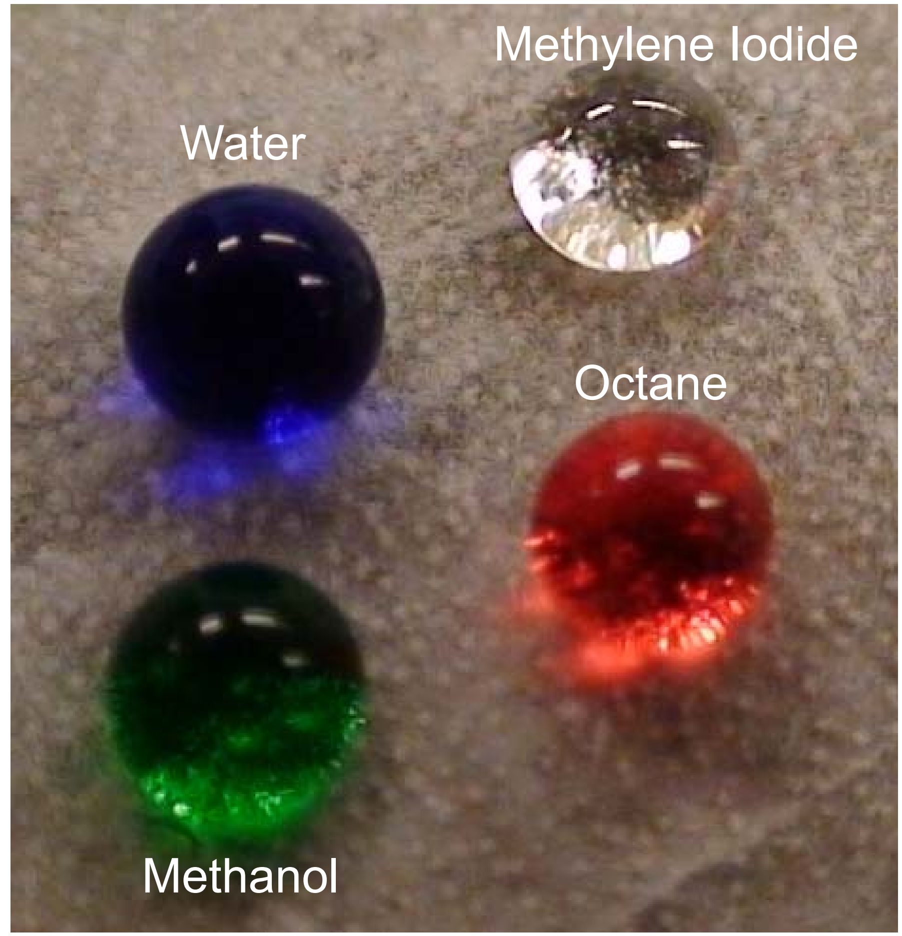
Herminghaus, *Euro. Phys. Lett.* (2000), Tuteja *et al. Science (*2007*);* Tuteja et al., PNAS, (2008*).*

DISTRIBUTION A. Approved for public release; distribution unlimited.

Designing Omniphobic Surfaces

- **Constructing super-repellent surfaces**
  - Three key ingredients



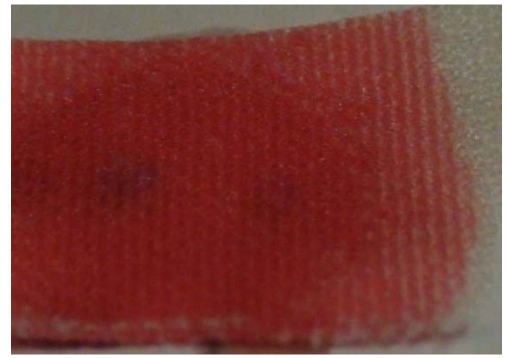


PMMA + 44 wt% POSS
electrospun coating (beads on a string) morphology

DISTRIBUTION A. Approved for public release; distribution unlimited.

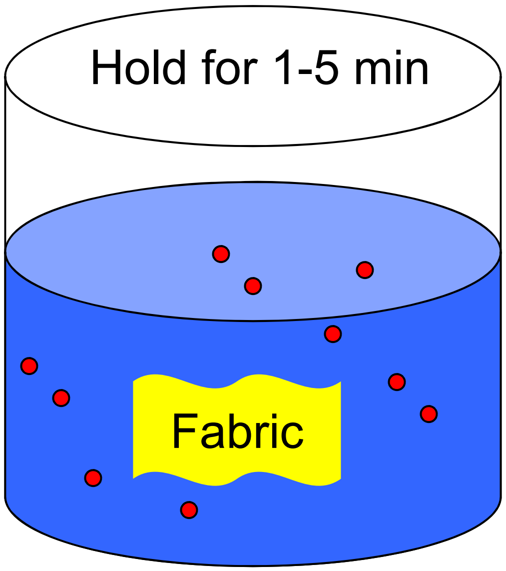
The Dip-Coating Process

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



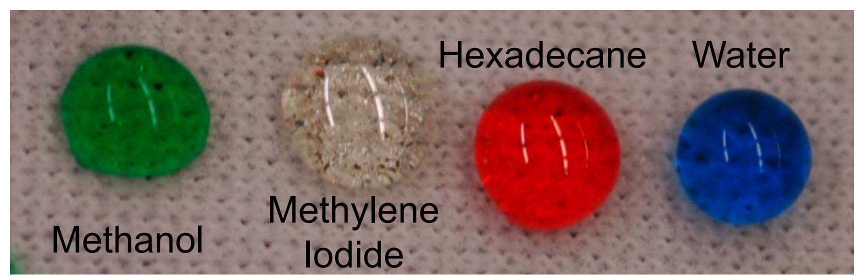
Before

Dip



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

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

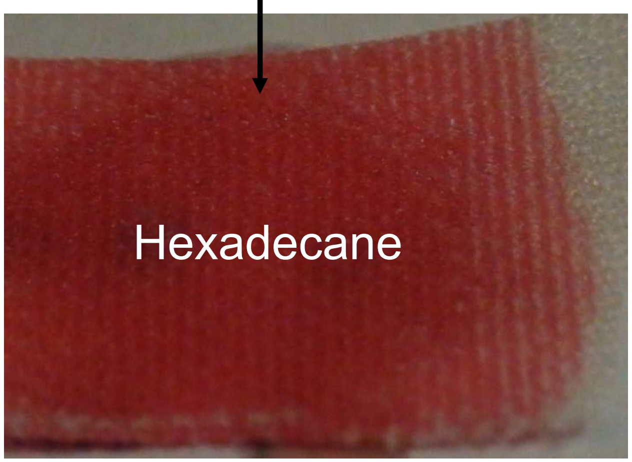


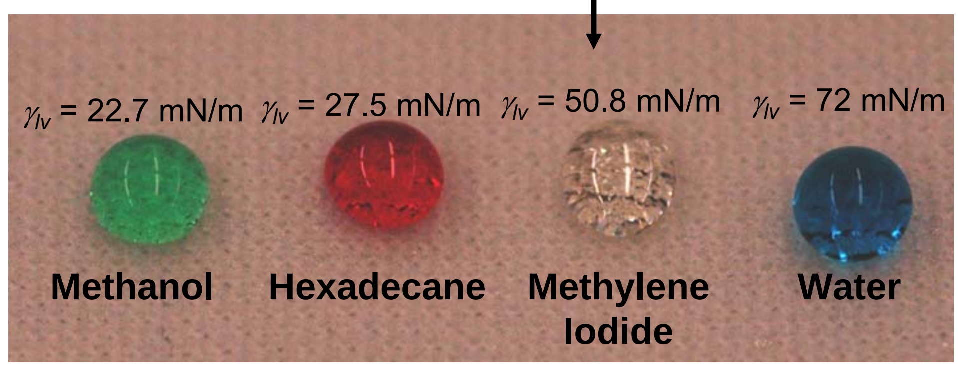
After dip-coating with a solution of fluorodecyl POSS

Dip-Coated Polyester Fabric

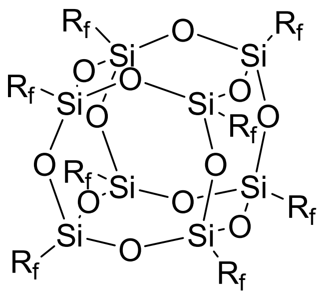
Before coating

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

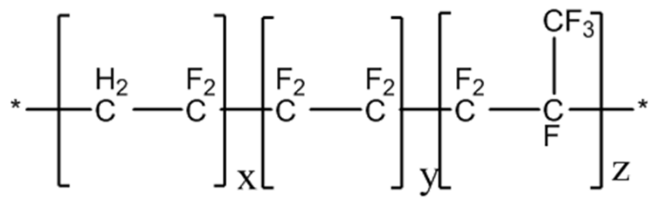




Dip-coating process for conformal coating of textured surfaces



R_f = $-CH_2-CH_2-(CF_2)_7-CF_3$
Fluorodecyl POSS
$\gamma_{sv} \approx 8$ mN/m

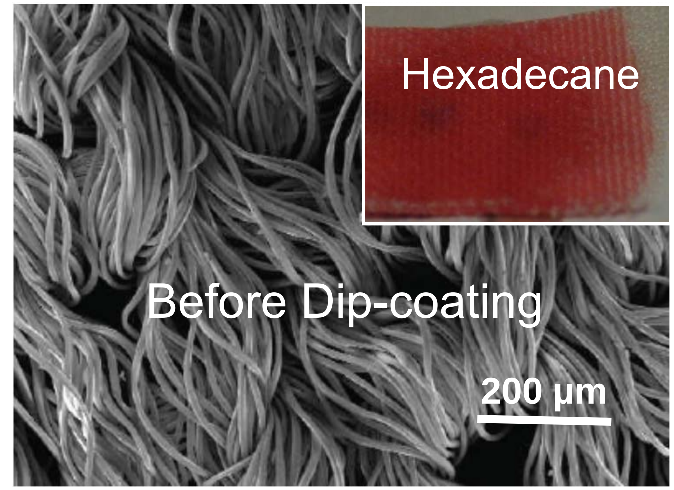


Tecnoflon® (BR9151)
Fluoro-elastomer from Solvay-Solexis
$\gamma_{sv} \approx 18$ mN/m

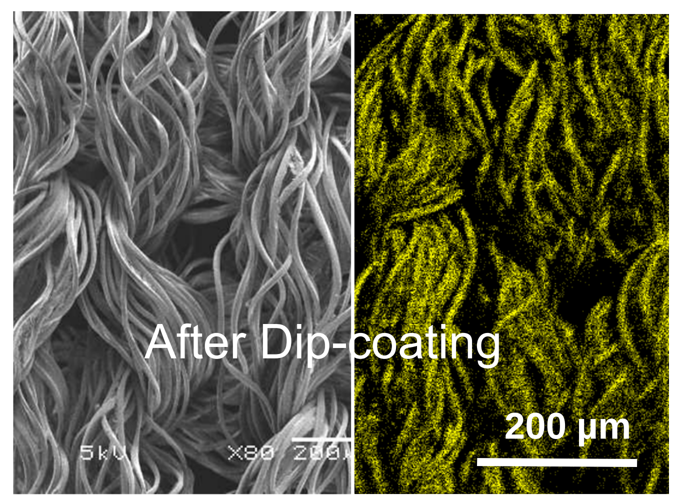
50:50 mixture, total solids = 10 mg/ml

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



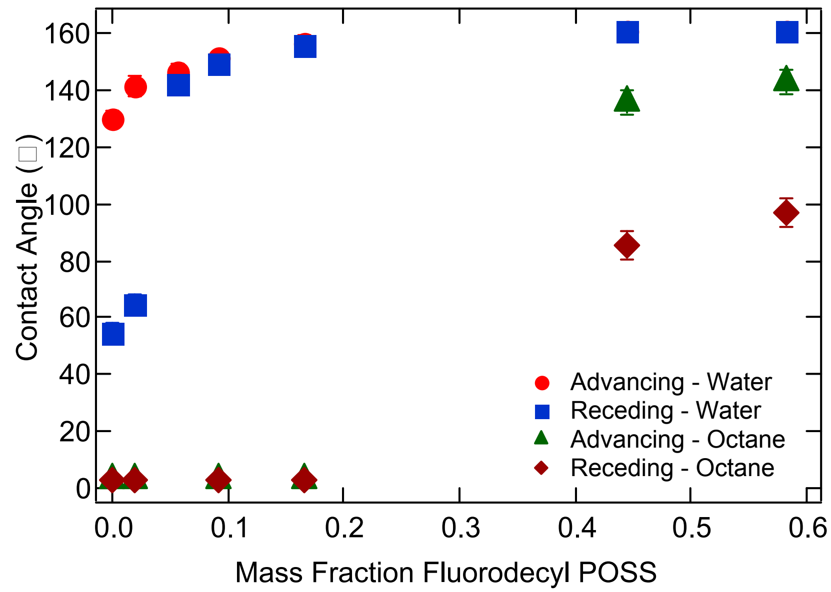
DISTRIBUTION A. Approved for public release; distribution unlimited.

Superhydrophobic/Superoleophilic

Designing Superoleophobic Surfaces

Anish Tuteja,[1] Wonjae Choi,[2] Minglin Ma,[1] Joseph M. Mabry,[3] Sarah A. Mazzella,[3] Gregory C. Rutledge,[1] Gareth H. McKinley,[2]* Robert E. Cohen[1]*

Superhydrophobic
Superoleophilic



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

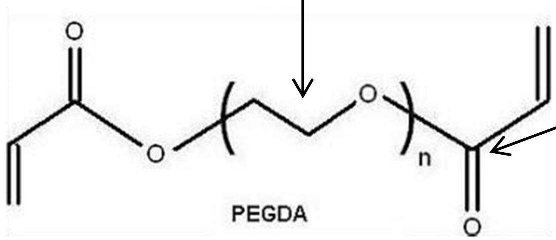
Science, **2007**, *318*, 1618.

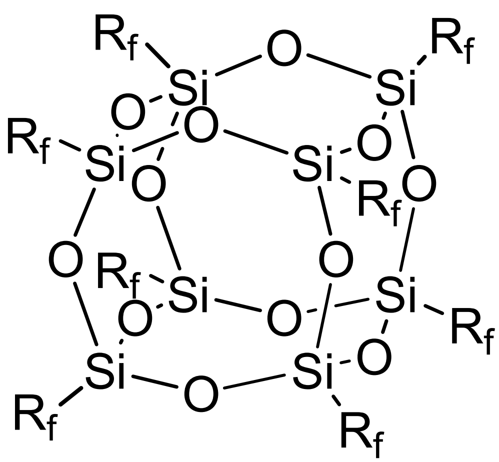
DISTRIBUTION A. Approved for public release; distribution unlimited.

PEGDA + Fluorodecyl POSS

Can hydrogen bond with water

Photo-crosslinkable





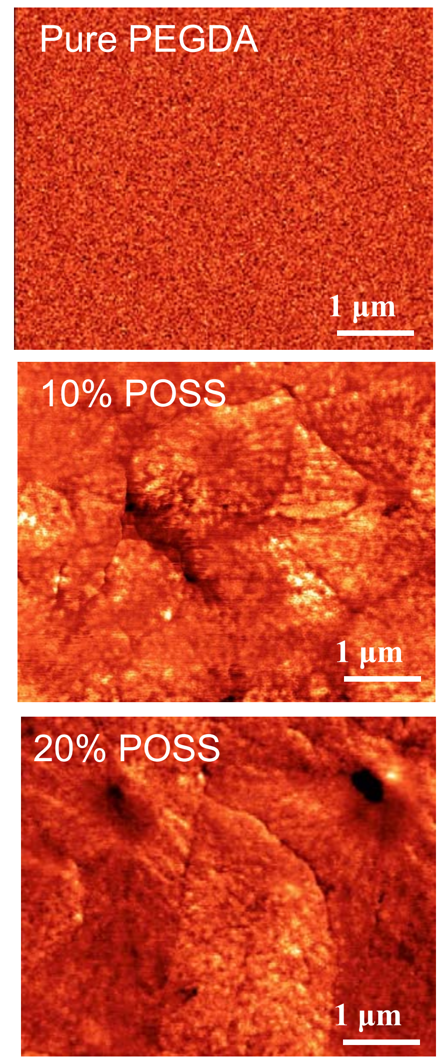
$R_f = -CH_2-CH_2-(CF_2)_7-CF_3$

Fluorodecyl POSS

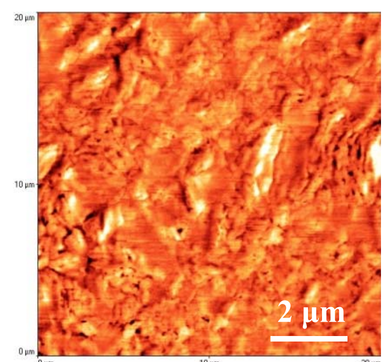
$\gamma_{sv} \approx 8$ mN/m

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

AFM Phase images of spin-coated PEGDA + POSS films

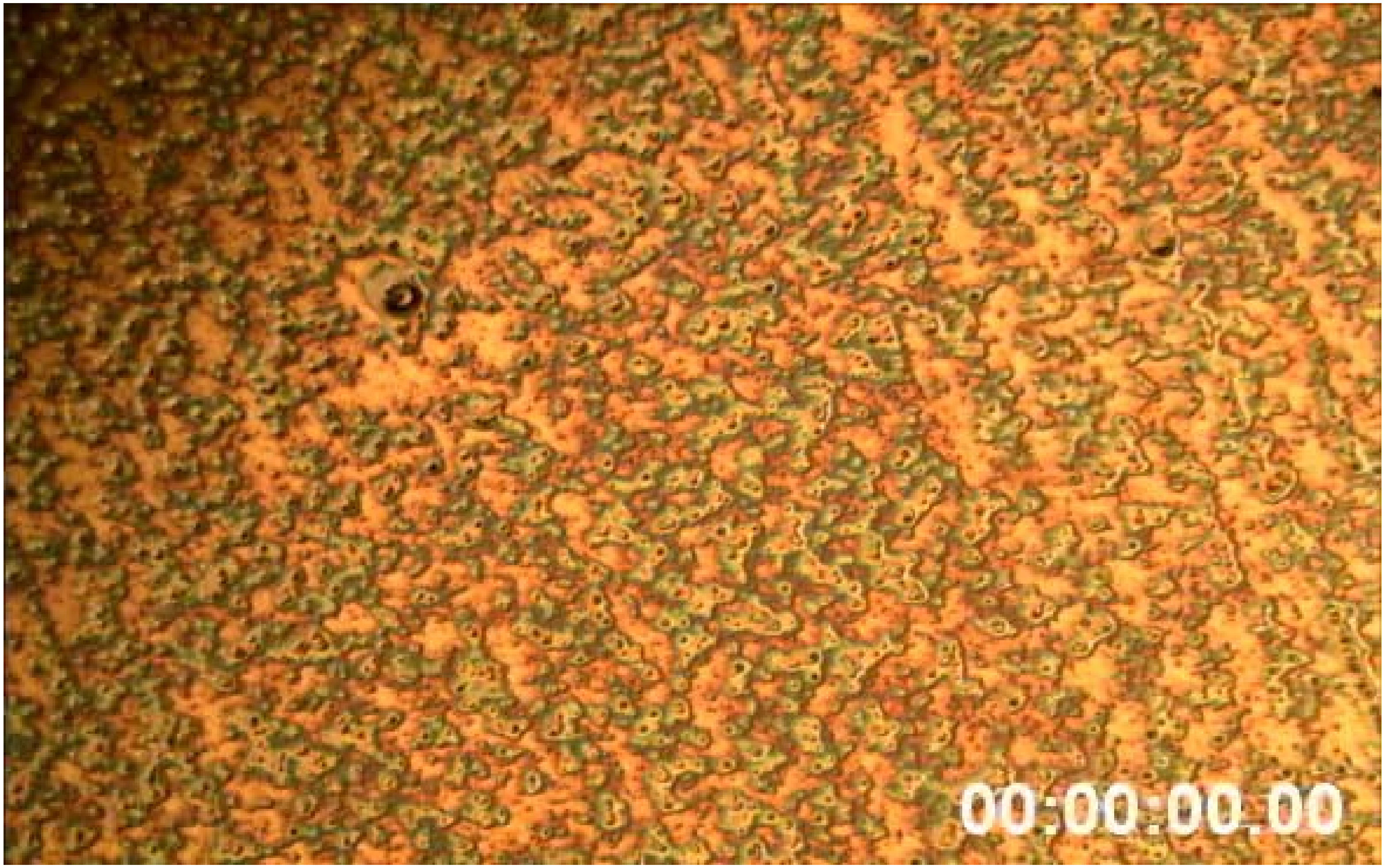


20% POSS
Under water



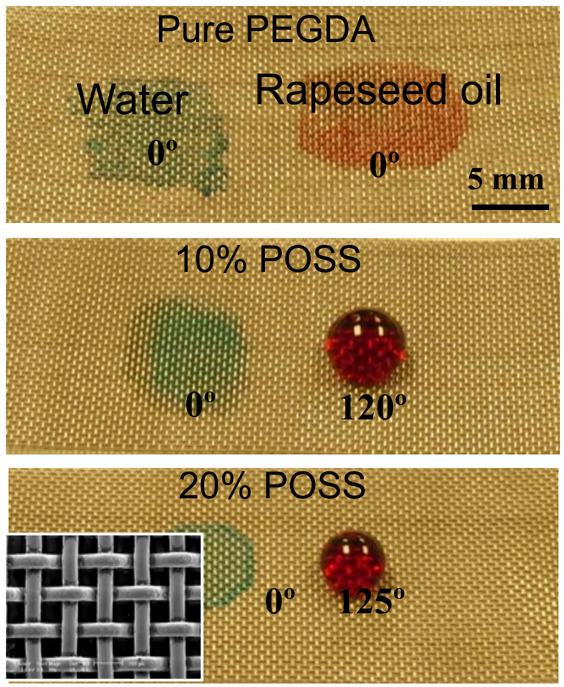
DISTRIBUTION A. Approved for public release; distribution unlimited.

PEGDA + Fluorodecyl POSS

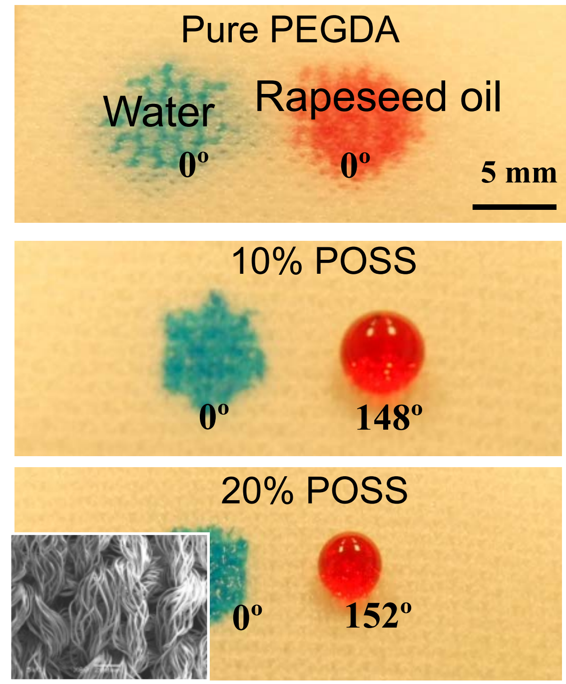


PEGDA + fluorodecyl POSS blends

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



Stainless Steel Wire Mesh

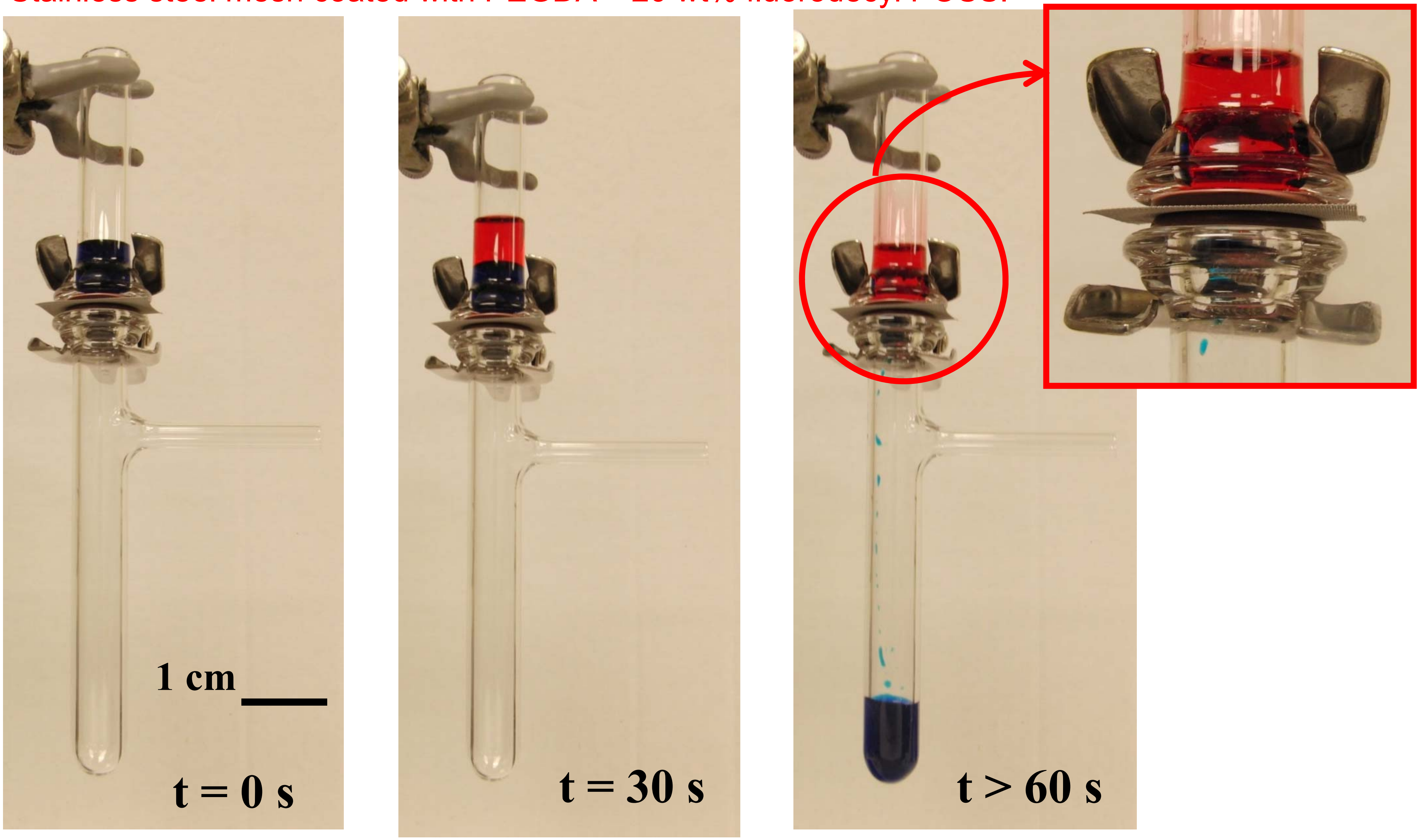


Commercial Polyester Fabric

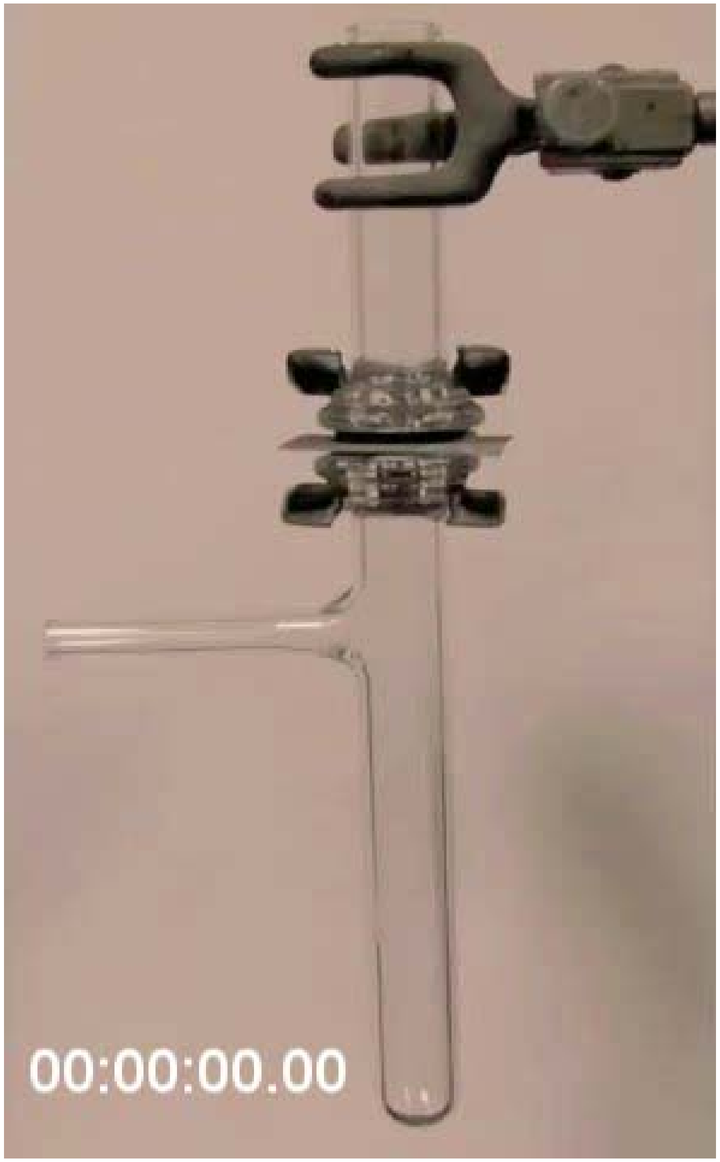
PEGDA surface reconfiguration leads to superhydrophilic behavior.

Free oil – water separation

Stainless steel mesh coated with PEGDA + 20 wt% fluorodecyl POSS.

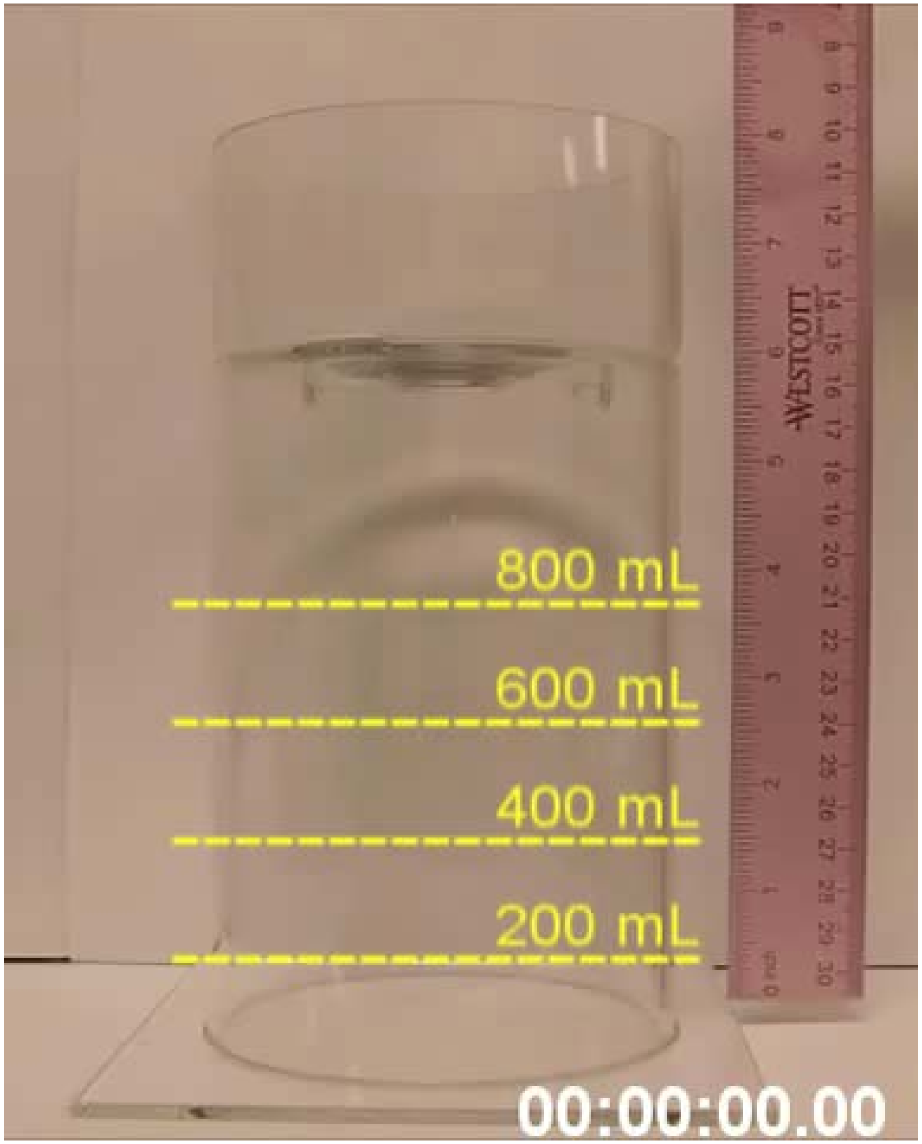


Free oil – water separation



DISTRIBUTION A. Approved for public release; distribution unlimited.

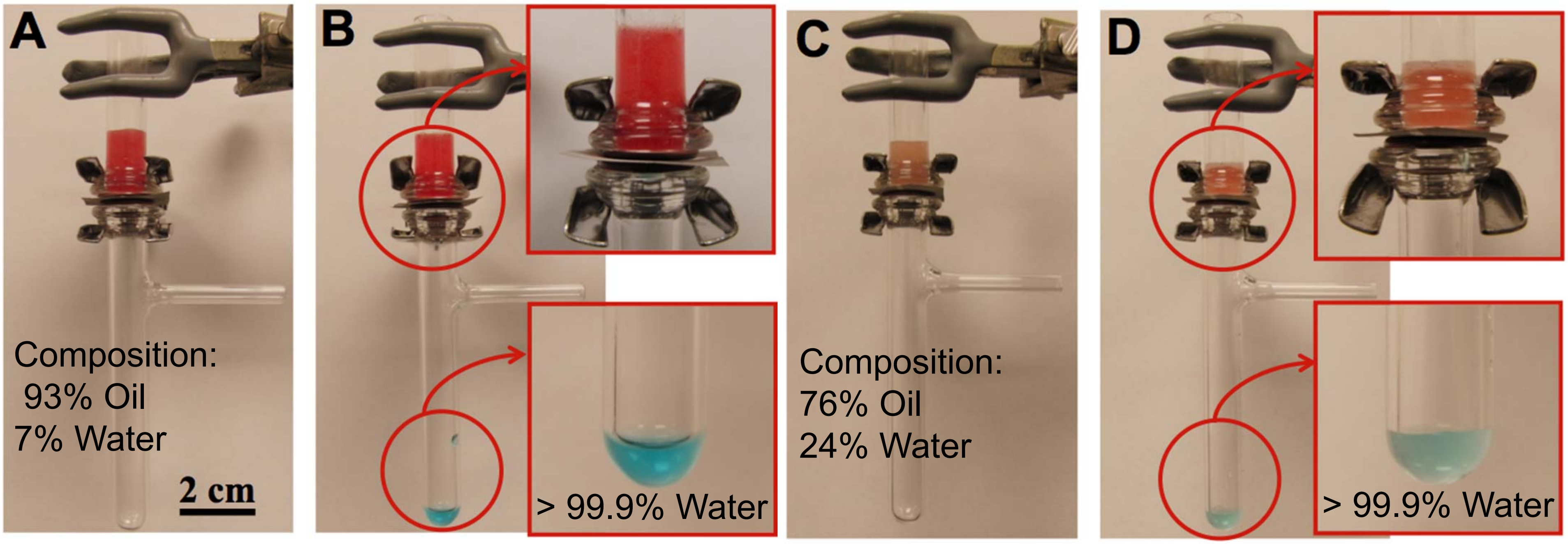
1-Liter scale separation



Separation of Oil-Water Emulsions

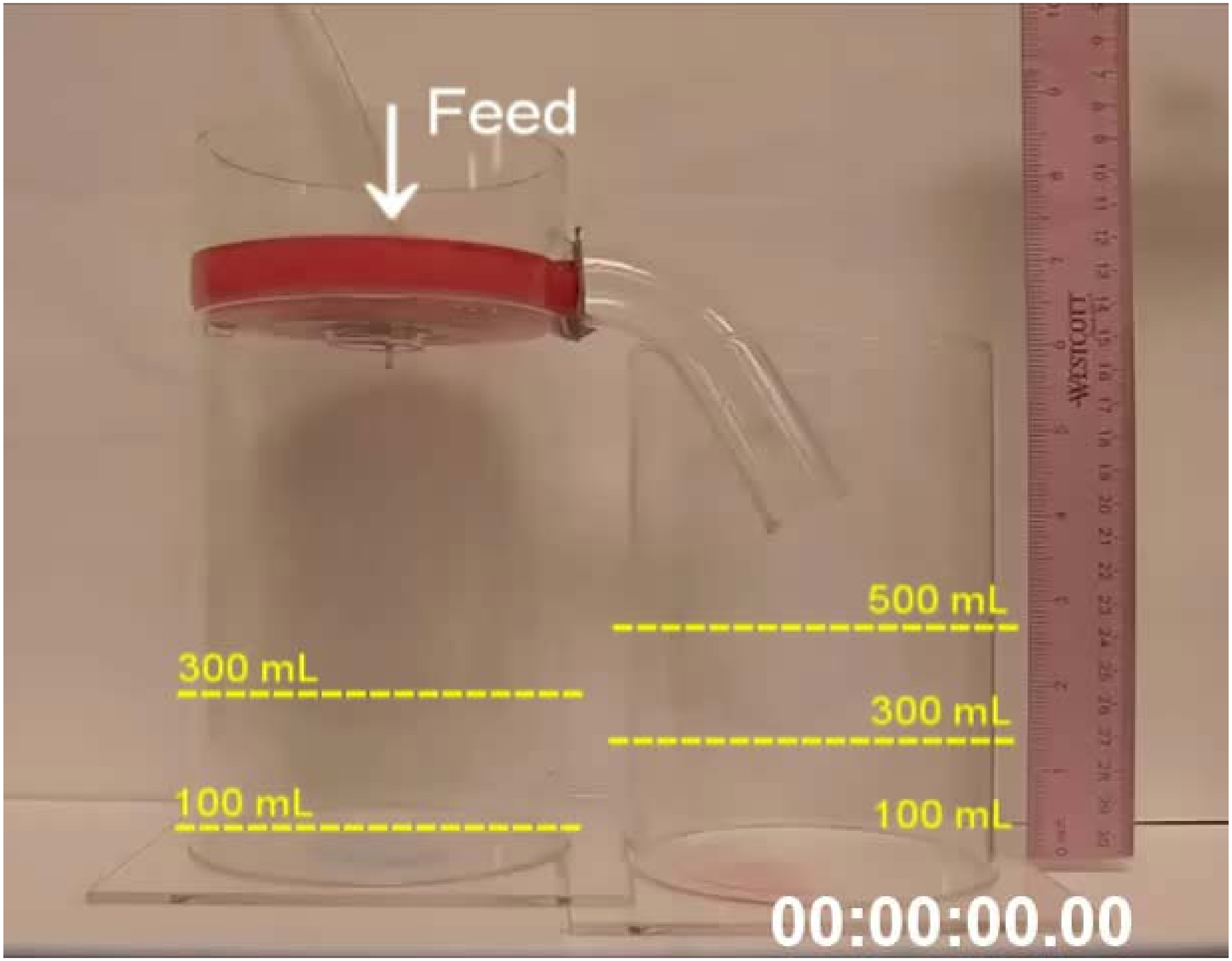
Water-in-Oil Emulsion

Oil-in-Water Emulsion



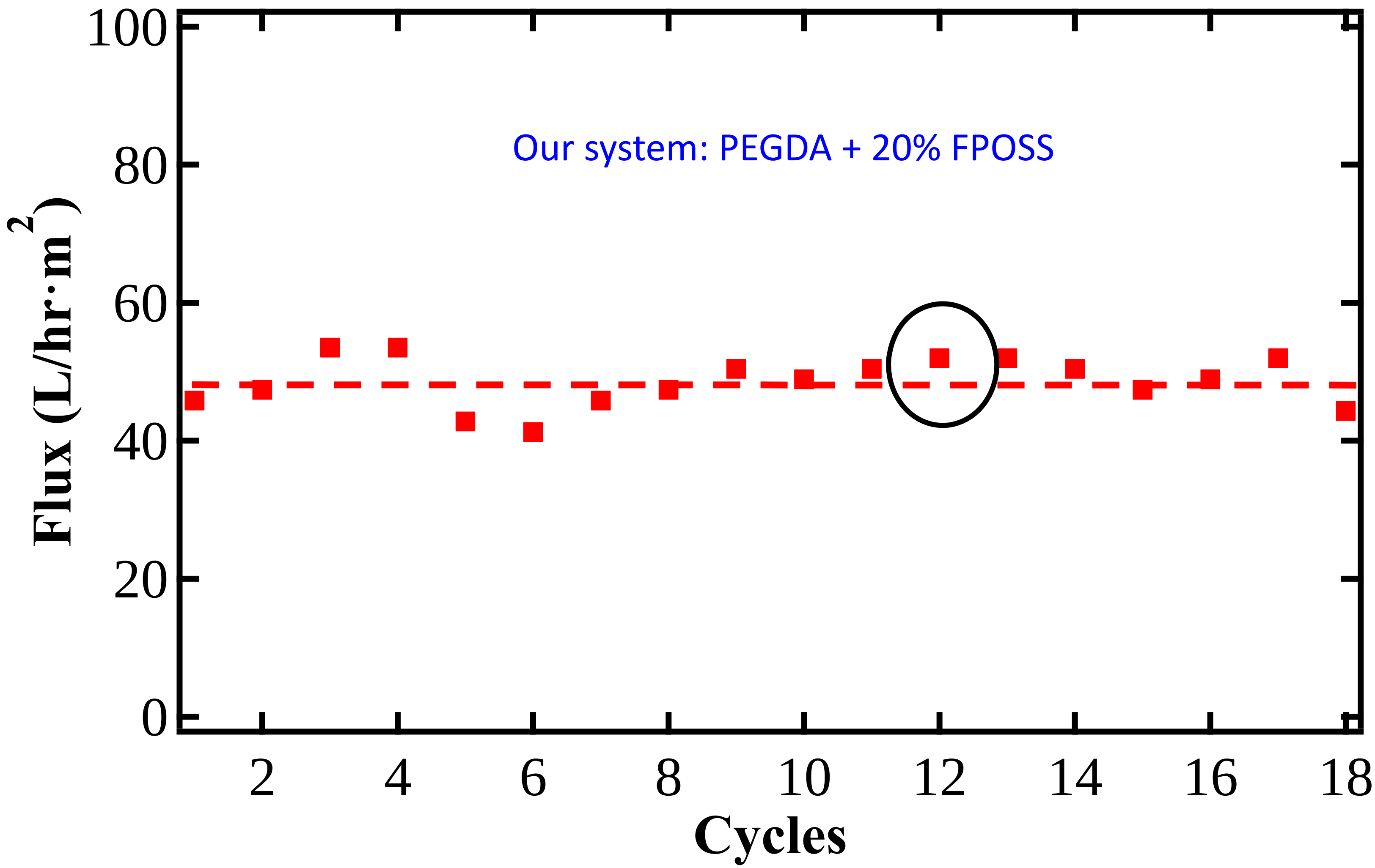
A simple, scalable, gravity-based system for the separation of both oil-in-water and water-in-oil emulsions. This is one of the first gravity-based systems to achieve such high emulsion separation efficiencies.

Gravity-driven, continuous-flow device

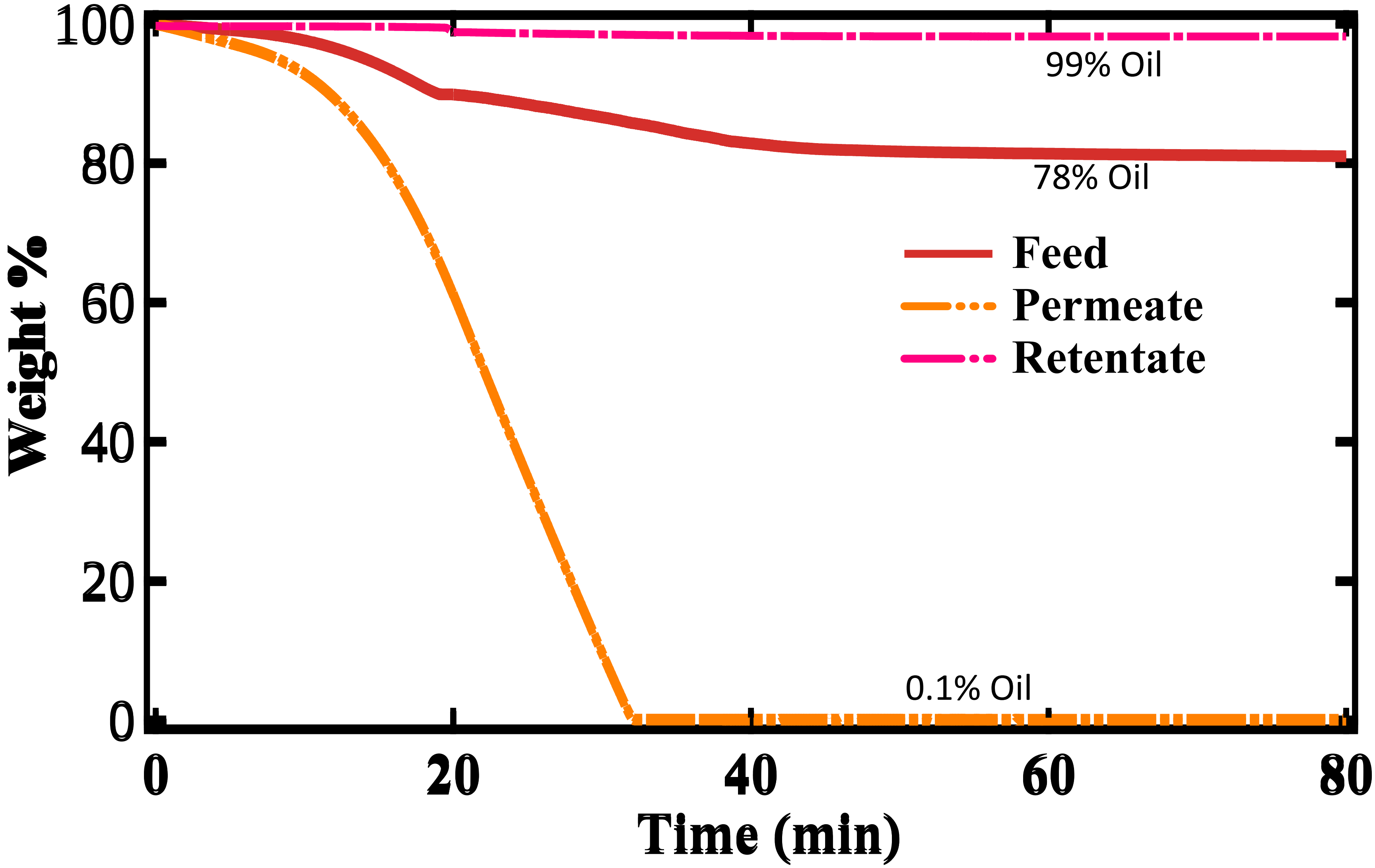


DISTRIBUTION A. Approved for public release; distribution unlimited.

Oil-Water Emulsion Separation



Separation Efficiency



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.

Acknowledgements

Professor Anish Tuteja

Oil/Water Separation Membranes

Polymer Working Group

Fluorinated POSS

Financial Support

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

Availability
- Logistics / Transportation
- Feedstock Variance

Performance
- Reusability / Durability
- Composition Optimization

Raw Material Cost
- Refining Process
- Fluctuations in fuel source and economy

Fuel Cost

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

Removal of Aromatics
- Udex
- Sulfolane
- Lurgi Arosolvan

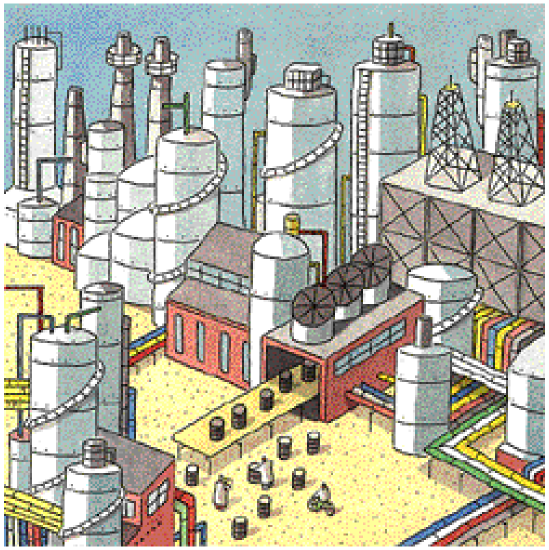
Sulfur Removal
- Hydrodesulfurization

Dye removal

Novel Liquid-Liquid Extraction Process

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

Vision



To develop the capability to produce high-performance military fuels at reduced cost with increased availability.

Thesis: Use ℓ/ℓ extraction to provide improvements in several critical areas

- Reduced supply-chain logistics
- Decreased risk of supply interruption

Availability

- Reduced coking
- I_{sp} improvement
- Improved thermal stability

Performance

- Reduced logistics cost
- Less Expensive feed streams

Cost

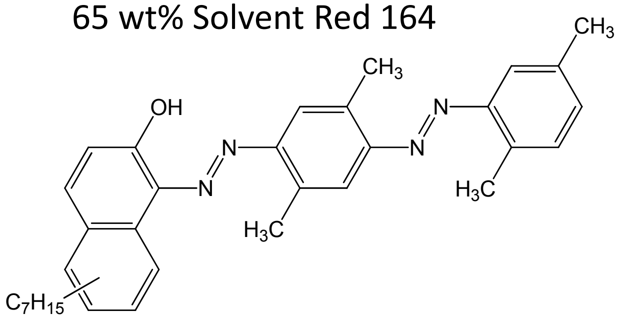
Objective: Utilize liquid/liquid extraction process to improve performance, increase availability, and reduce cost of RP by producing these fuels from less expensive feed streams.

Undesirables in RP-1

Oil Red B4 (ORB4)

Dye in RP-1

65 wt% Solvent Red 164



15-30 wt% xylene

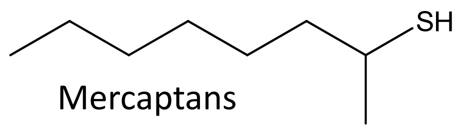
5-10 wt% ethylbenzene

Detrimental to Thermal Stability!

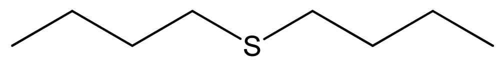
Sulfur Compounds

Present in RP-1

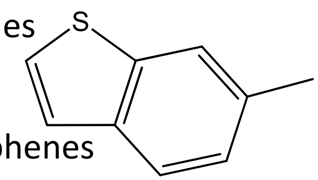
Concentration varies



Mercaptans



Sulfides



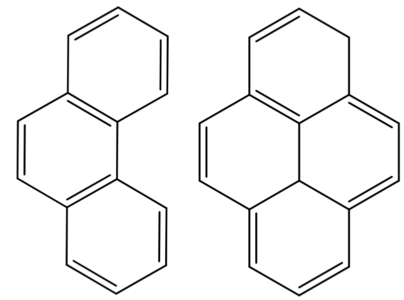
Thiophenes

Catalysts for Coking Reactions

Aromatics

Present in RP-1

Concentration varies

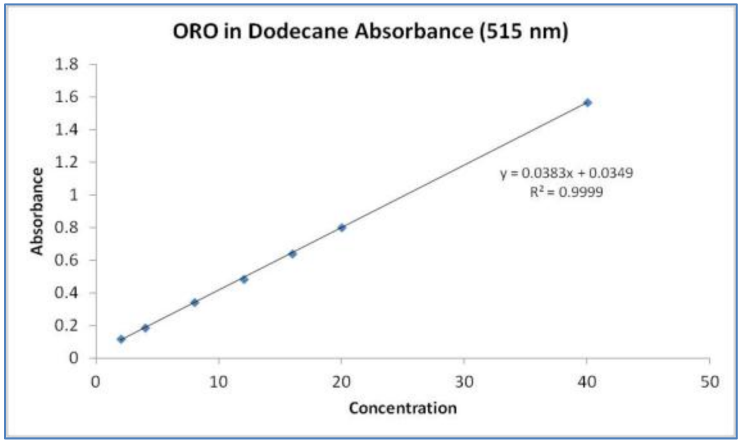


Detrimental to Performance

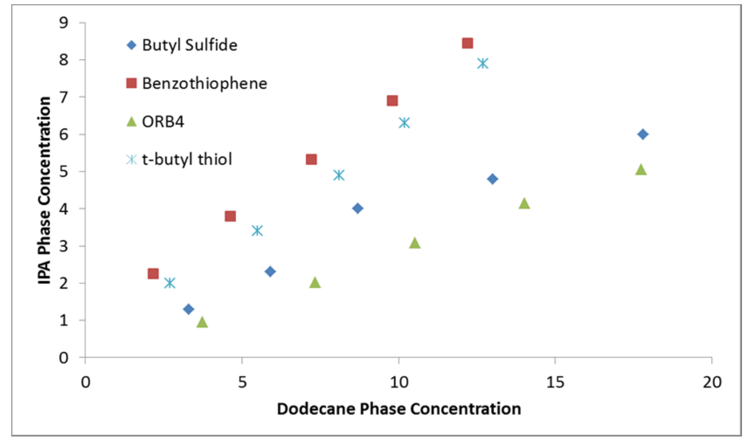
RP-2 is expensive and requires an additional supply chain, which also consumes resources and may be put at risk due to unforeseen circumstances.

Removal from less expensive feed streams will increase availability, reduce supply risk, reduce cost, and improve performance.

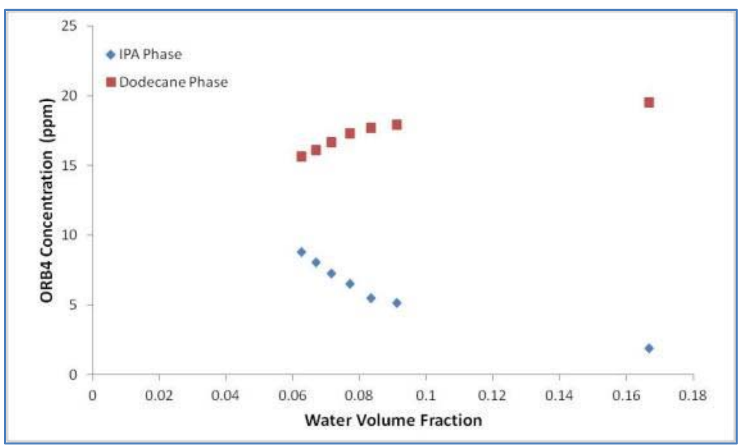
Extraction Parameter Determination



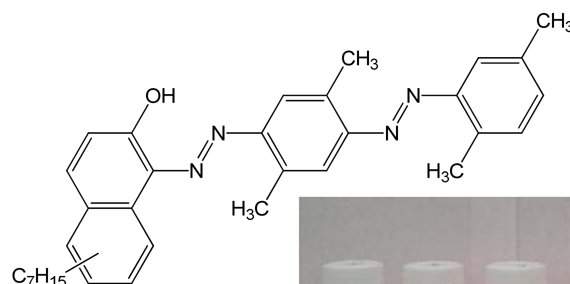
Visible spectroscopy was used to determine concentration of dye from 2-40 ppm.



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

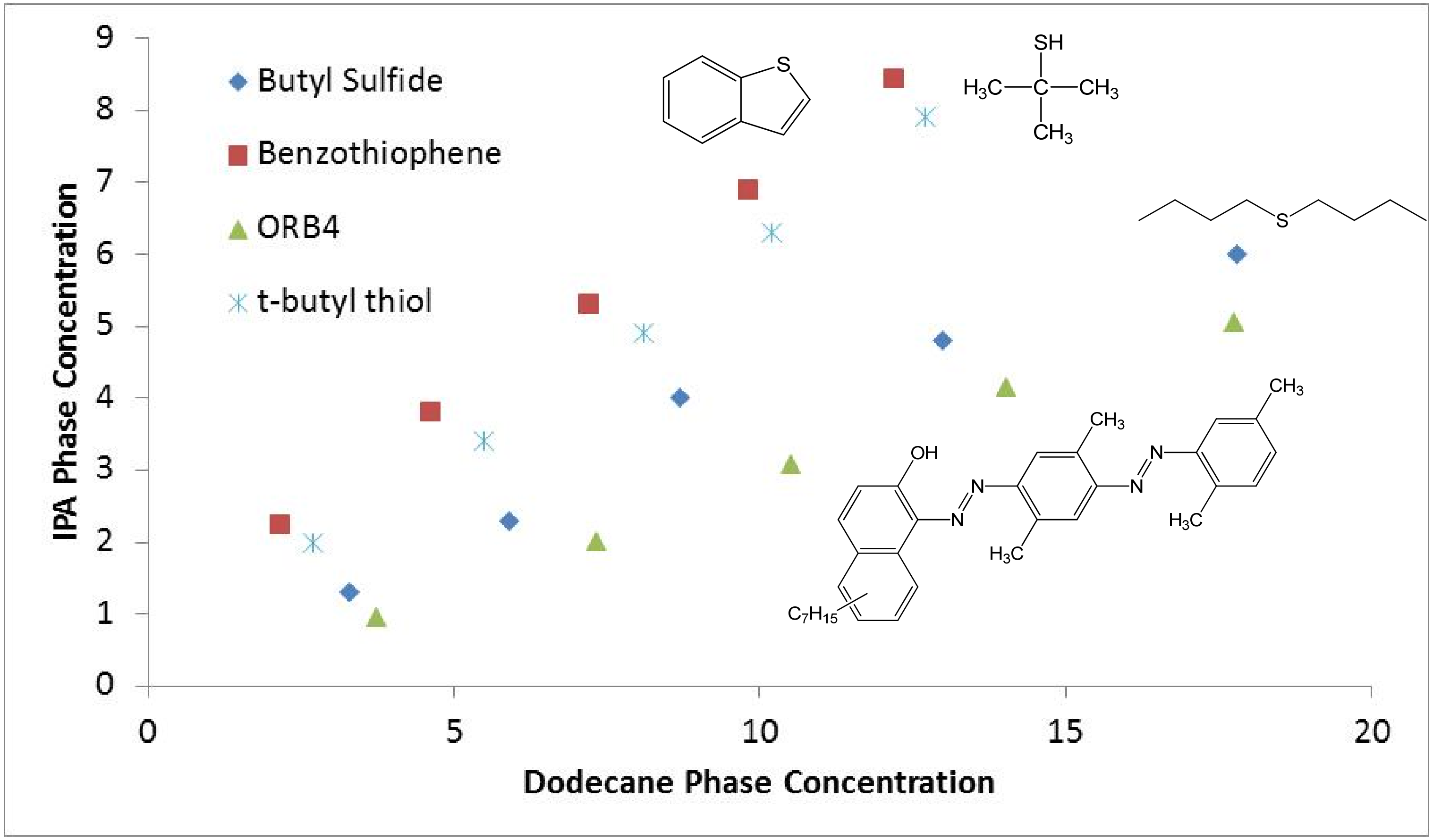


Higher IPA : Water ratio results in higher dye concentration.



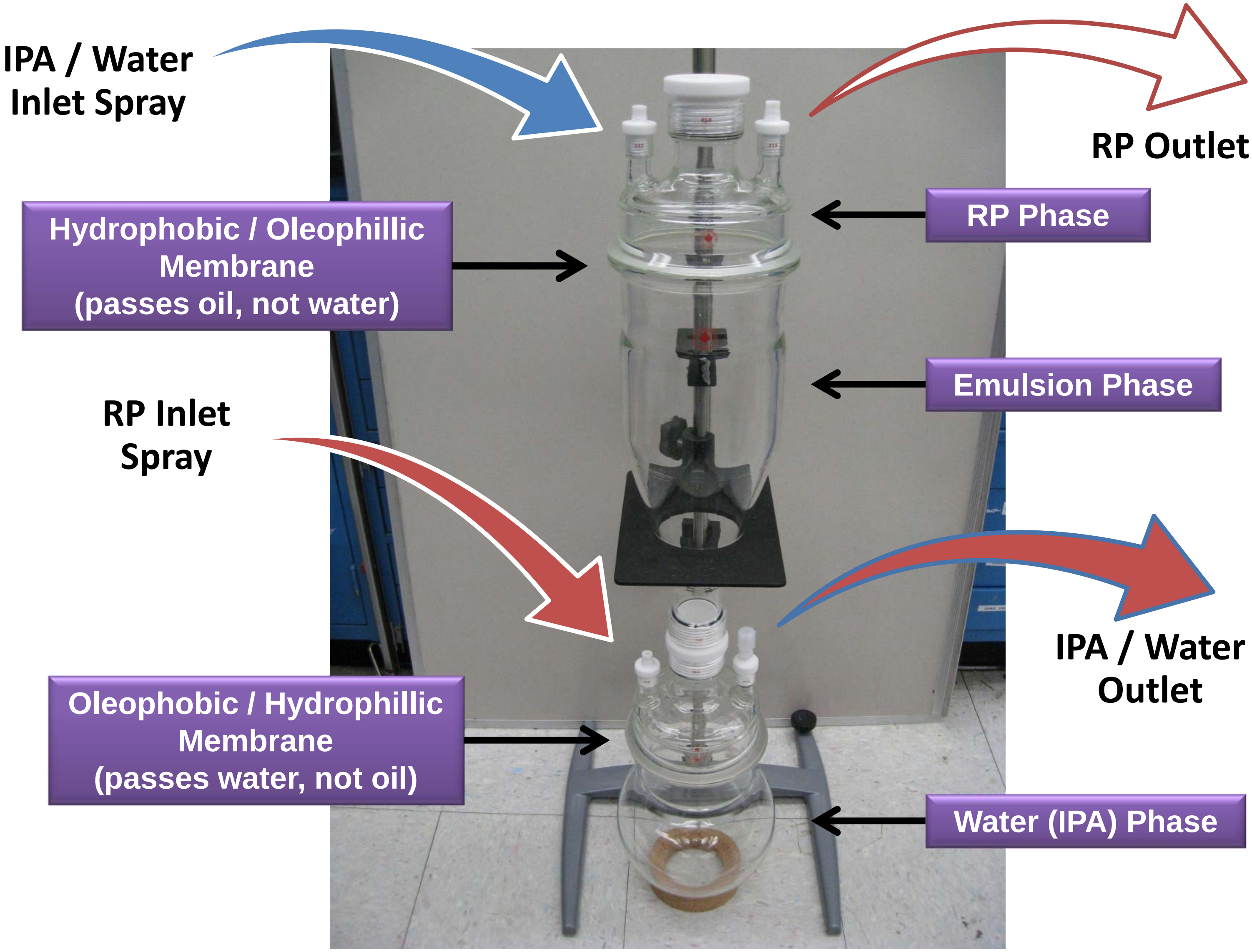
Optimum IPA : Water ratio is ~13 : 1 based on small scale extractions.

Extraction Curves



Equlibrium curve for compounds extracted from dodecane with IPA:water 10:1 v:v ratio

Extraction Apparatus



Extraction of Sulfur from RP-1

Sulfur Compounds by GC-SCD (Sulfur Speciation)	Concentration (ppm)
C2 Thiophenes	<0.1
C3-C4 Thiophenes	1.6
C5 Thiophenes	6.3
C6 Thiophenes	6.1
C7 Thiophenes	5.8
C8-C9 Thiophenes	4.9
C10 Thiophenes	1.3
C11 Thiophenes	0.9
C12+ Thiophenes	2.0

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

Sulfur Compounds by GC-SCD (Sulfur Speciation)	Concentration (ppm)
C2 Thiophenes	0.3
C3-C4 Thiophenes	1.4
C5 Thiophenes	3.7
C6 Thiophenes	3.5
C7 Thiophenes	4.1
C8-C9 Thiophenes	2.9
C10 Thiophenes	0.6
C11 Thiophenes	0.6
C12+ Thiophenes	<0.1

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

Dr. Greg Yandek
Dr. Andrew Guenthner
Dr. Josiah Reams
Dr. Tim Haddad
Mr. Jason Lamb
Dr. Jeff Alston

Mr. Jacob Marcischak
Mr. Kevin Lamison
Dr. Joe Mabry
Lt Diane Fernandez
Mr. Michael Ford

AFRL/RQR

AFOSR

Acknowledgements

Professor Anish Tuteja

Oil/Water Separation Membranes

Polymer Working Group

Fluorinated POSS and Extraction Work

Financial Support

Air Force Office of Scientific Research

Air Force Research Laboratory, Aerospace Systems Directorate


QUESTIONS?
U.S. AIR FORCE