Sugar-Based Photoacid Generators (“Sweet” PAGs):

Environmentally Friendly Materials for Next Generation Photolithography

(*Task Number: 425.029*)

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PIs:

- **Christopher K. Ober, Materials Science and Engineering, Cornell University**
- **Reyes Sierra, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Lila Otero, PhD candidate, Chemical & Environmental Engineering, UA**
- **Marie Krysak, PhD candidate, Materials Science & Engineering, Cornell University**

Undergraduate Students:

- **Lily Milner, Chemical & Environmental Engineering, UA**

Other Researchers:

- **Youngjin Cho, Postdoctoral Fellow, Materials Science & Eng., Cornell University**
- **Wenjie Sun, Postdoctoral Fellow, Chemical & Environmental Engineering, UA**

Cost Share (other than core ERC funding):

- **UofA GIGA fellowship (1 year) to Lila Otero.**

Objectives

- **Develop PFOS-free and environmentally friendly PAGs with superior imaging performance. The novel PAGs will be based on biological units such as sugars and cholic acids for chemically amplified resist application**

- **Identify modeling tools to predict the environmental fate of novel PAGs**

- **Evaluate the environmental aspects of new PAGs**

ESH Metrics and Impact

1. **Reduction in the use or replacement of ESH-problematic materials**

   Complete replacement of perfluorooctanesulfonate (PFOS) structures including metal salts and photoacid generators in photoresist formulations.

2. **Reduction in emission of ESH-problematic material to environment**

   Develop new PAGs that can be readily disposed of in ESH friendly manner.

3. **Reduction in the use of natural resources (water and energy)**

   New PAGs prepared using simple, energy reduced chemistry in high yields and purity to reduce water use and the use of organic solvents.

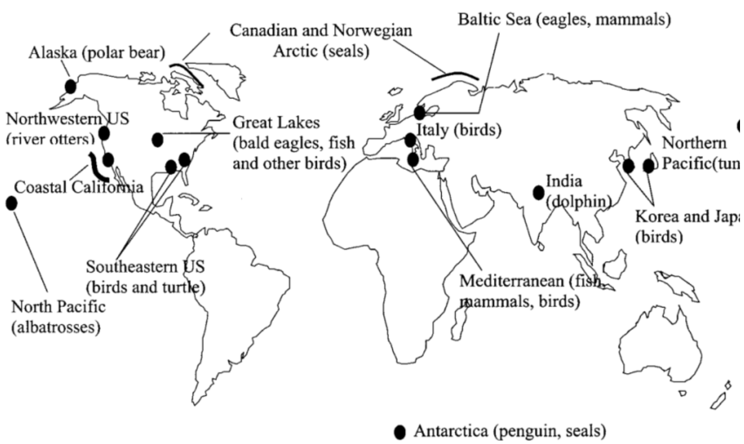
4. **Reduction in the use of chemicals**

   Reduction in the use of fluorinated chemicals.

PFOS is a Persistent, Toxic and Bioaccumulative (PBT) Contaminant

PFOS and PFOS-related materials are potentially environmentally hazardous

Global Distribution of PFOS in Wildlife



Environ. Sci. Technol. 2001, *35*, 1339.

PFOS in human blood

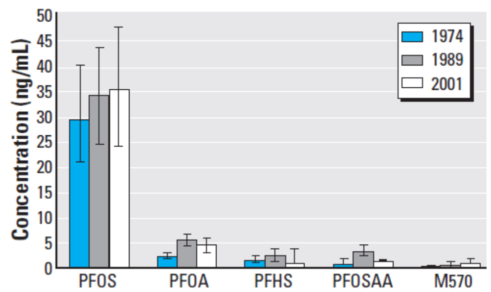


Figure 1. Median fluorochemical concentrations and IQRs for blood samples collected in Washington County, Maryland, from adults living in proximity in 1974 (n = 178 serum samples) and 1989 (n = 178 plasma samples) and in the county in 2001 (n = 108 serum samples; Olsen et al. 2003c).

Environ. Health Perspect. 2005, *113*, 539.

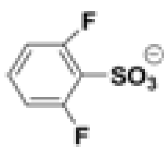
PFOS in drinking water

PFOS and other PFCs detected in drinking water resources worldwide

- PFOS banned for most application is the US and EU.
- Listed as chemical for regulation within the Stockholm Convention on Persistent Organic Pollutant
- EPA Provisional Health Advisory Levels for PFOS 200 ng L^{-1}

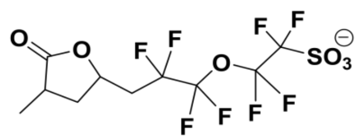
Environmental Compatibility of New Non-PFOS PAG Anions

Selected examples:



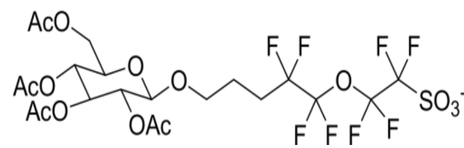
1st generation

(Aromatic structure)



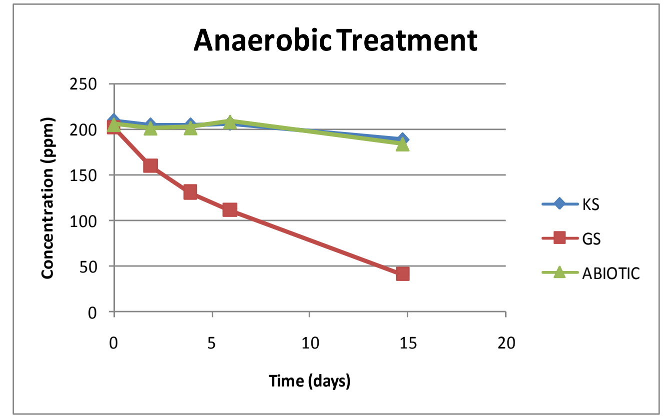
2nd generation

(Aliphatic structure)



3rd generation

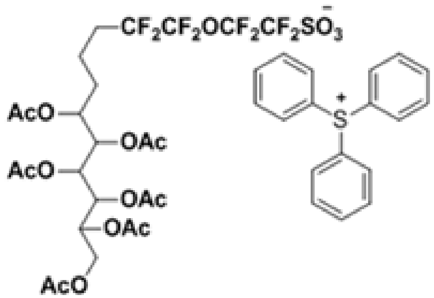
(Sugar structure)



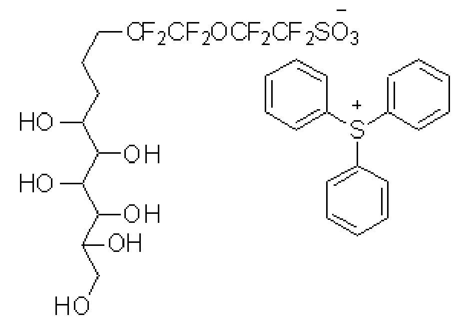
Degradation for 2nd generation PAG in anaerobic batch bioassays. (KS) Abiotic sterilized control; (GS) complete treatment with active sludge; (ABIOTIC) sterile, non-inoculated control.

- **1st Generation Non-PFOS PAGs: Low toxicity and low bioaccumulation potential but relatively persistent to microbial degradation.**
- **2nd Generation Non-PFOS PAGs: Preliminary results show that replacing the phenyl group with a UV-transparent alicyclic moiety increases the susceptibility of the PAG compound to biodegradation.**
- **3rd Generation Non-PFOS PAGs: Replacing with sugar and natural groups is expected to increase biodegradation.**

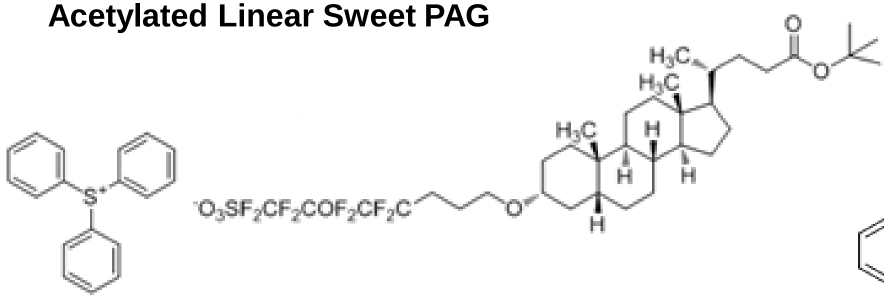
Environmentally Friendly PAGs



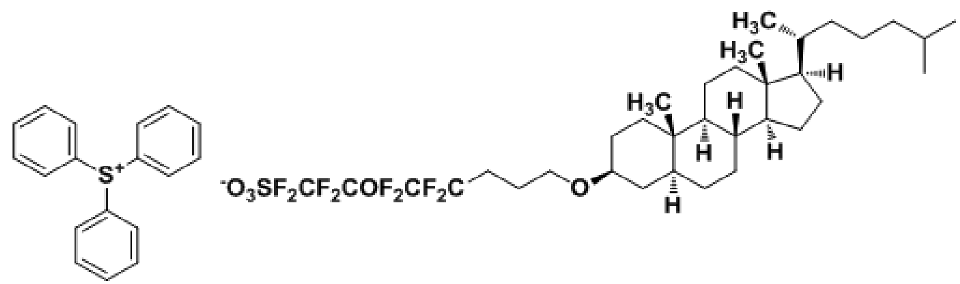
Acetylated Linear Sweet PAG



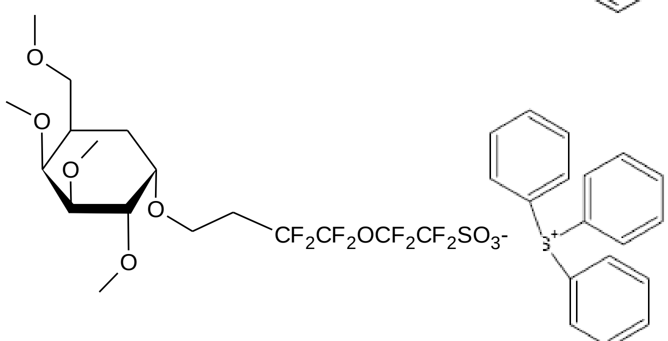
Linear Sweet PAG



Lithocholic Acid PAG

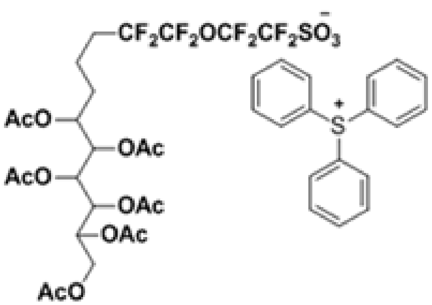


Dihydrocholesterol PAG



Methyl Sweet PAG

Linear Sweet PAG – Evaluation of Lithographic Performance

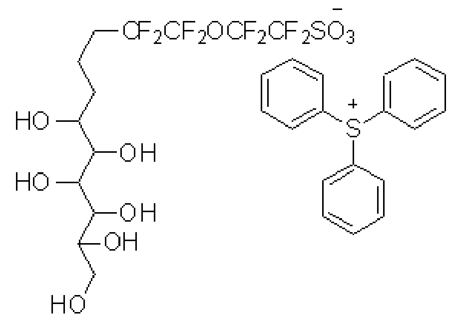


Tested with ESCAP resist

2.5mg PAG (5%)
1.0g Ethyl lactate (5% solution)

PAB: 130℃/60s
PEB: 130℃/60s

Development: 0.26 N TMAH/60s



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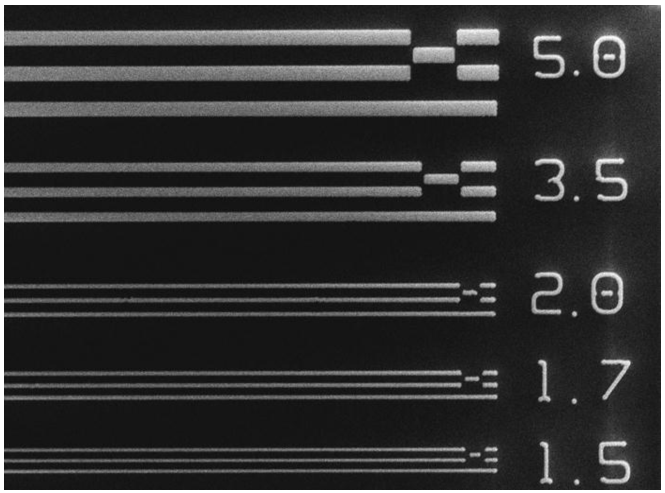
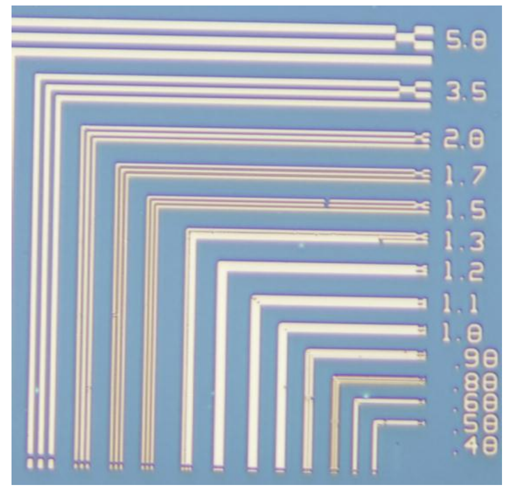


Dose: 20 mJ/cm^2 at 254nm



Dose: 20 mJ/cm^2 at 254nm

Solvent	PGMEA	Butanone	Ethyl lactate
Solubility of PAG	X	X	O

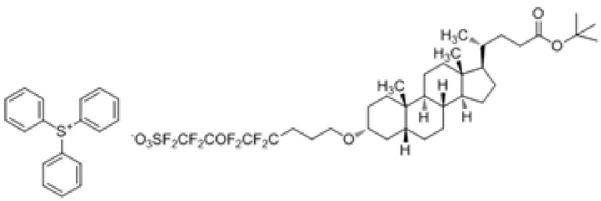
Solubility issues with linear sweet PAG

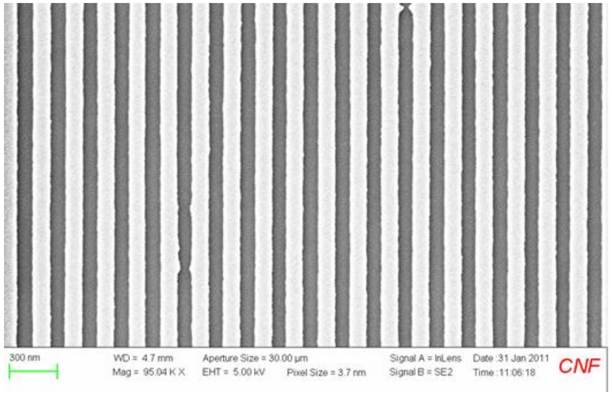
SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

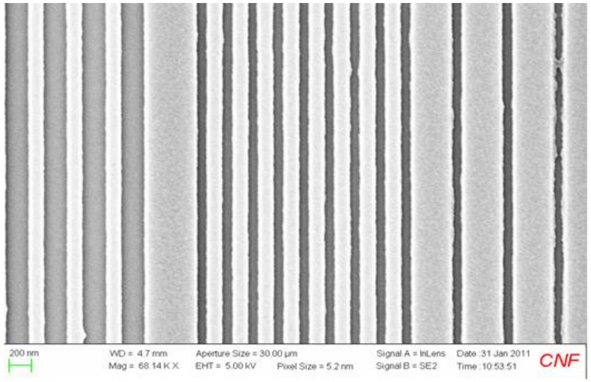
Lithocholic Acid PAG – Litho Performance vs. TPS-Nonaflate

100 nm dense lines

70 nm dense and isolated lines





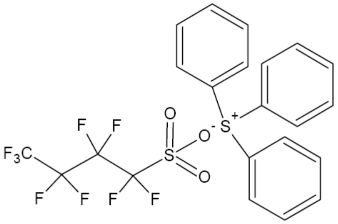


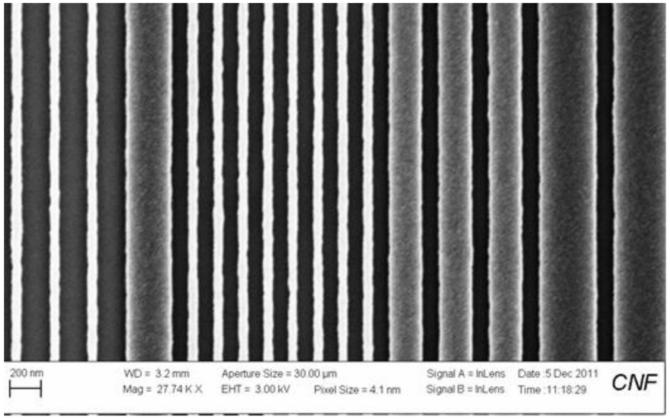
ESCAP resist with Lithocholic Acid PAG

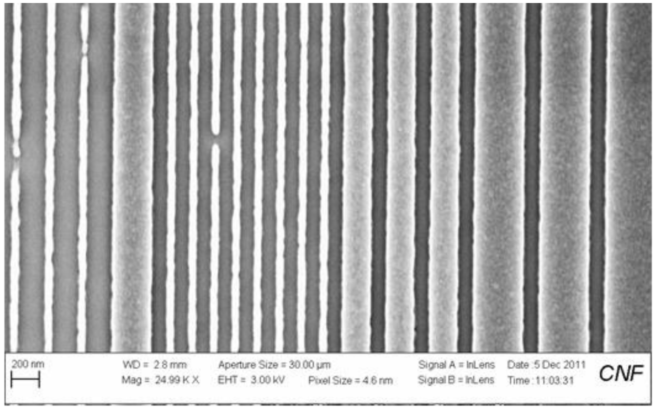
Dose = 175 µC/cm²

80 nm dense and isolated lines

70 nm dense and isolated lines





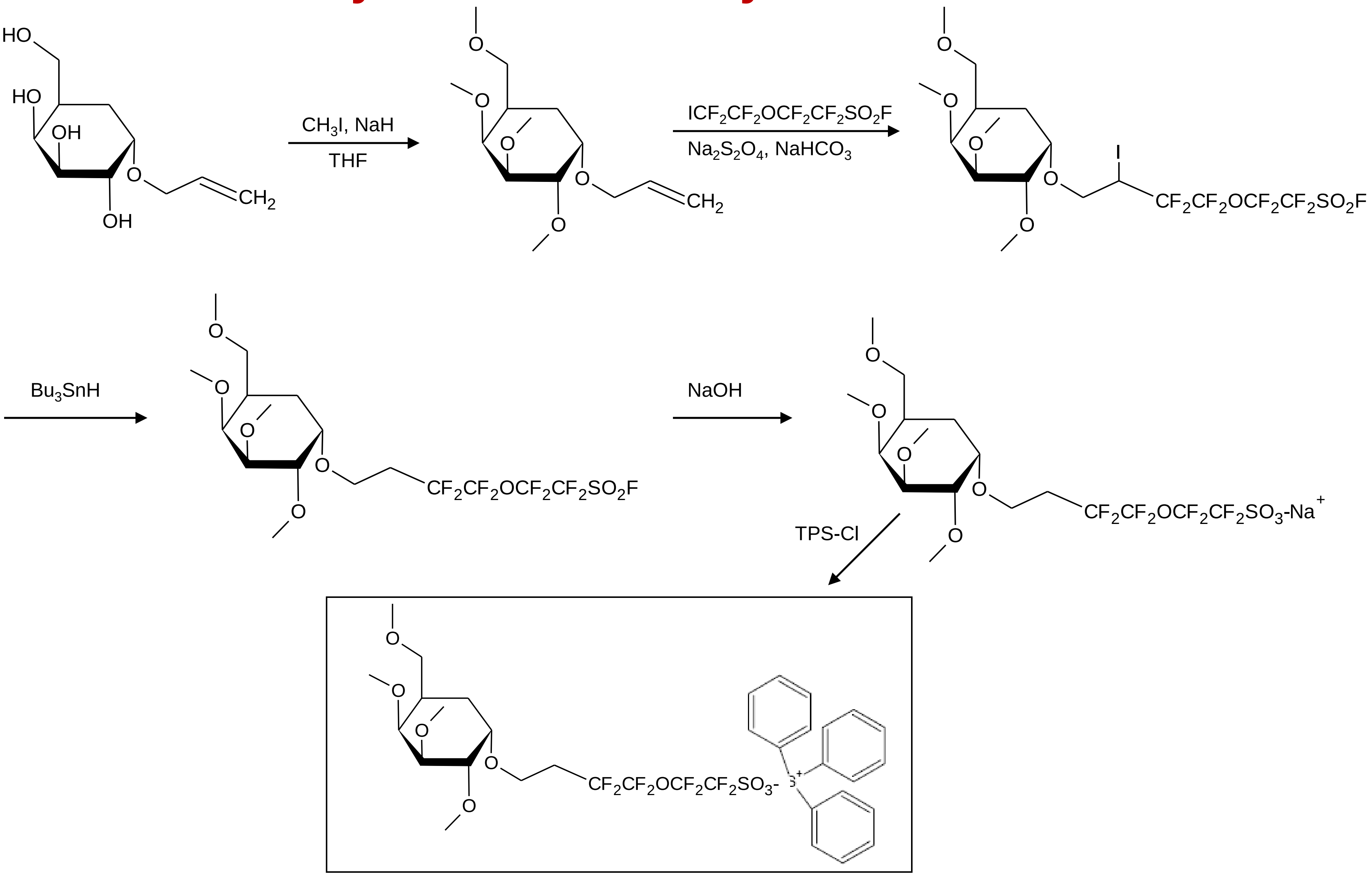


ESCAP resist with TPS-Nonaflate PAG

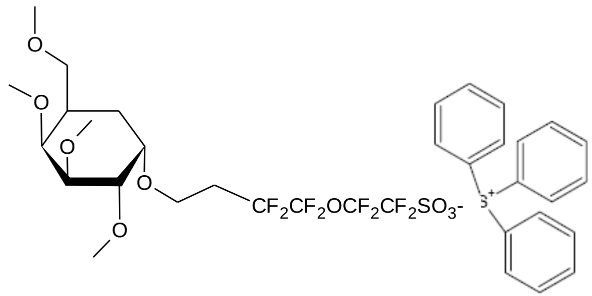
Dose = 10 µC/cm²

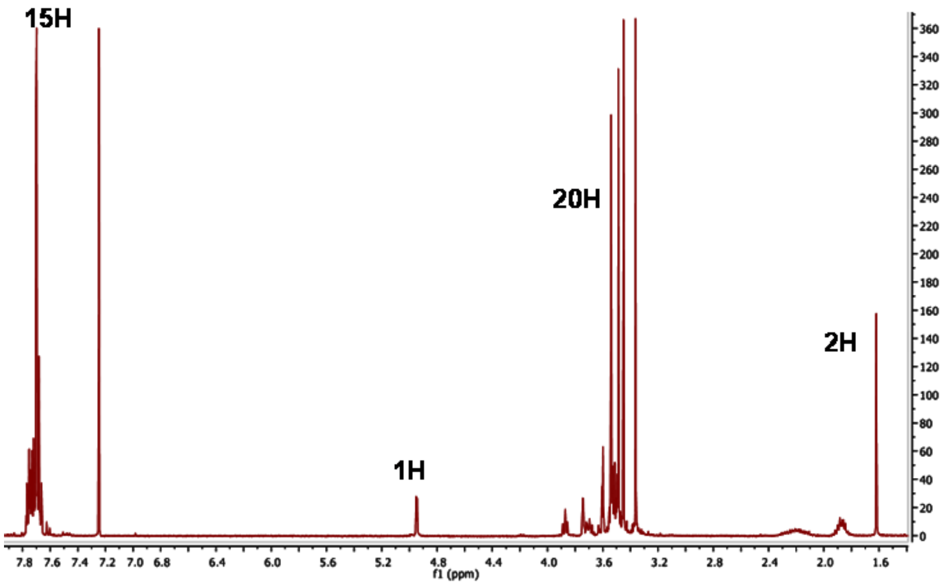
Resolution of lithocholic acid PAG is comparable to PFOS-containing PAG

Methyl Sweet PAG – Synthetic Scheme

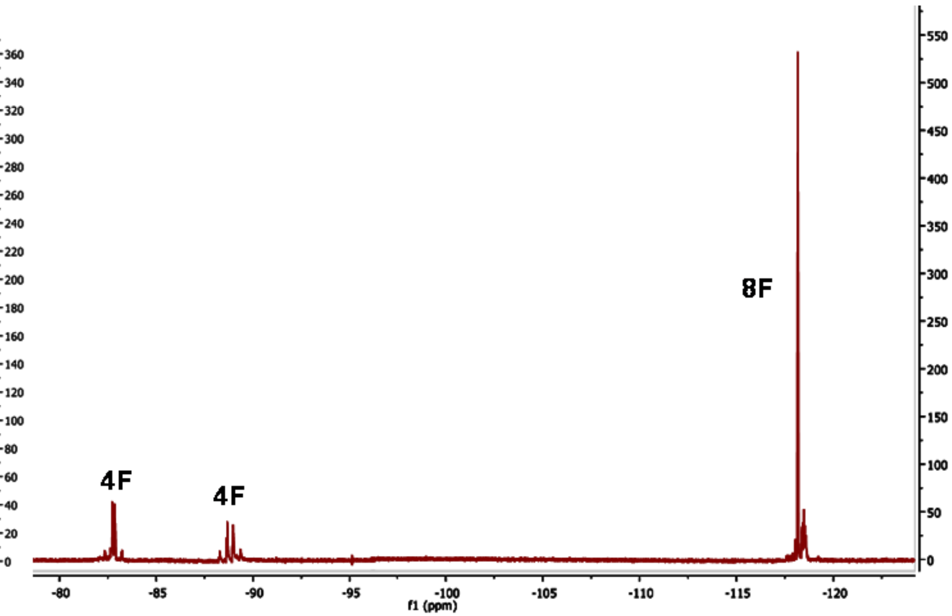


Methyl Sweet PAG – NMR Characterization





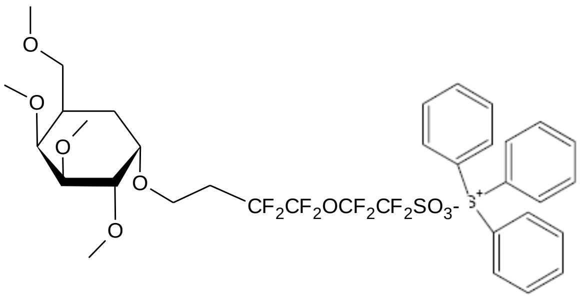
^{1}H NMR



^{19}F NMR

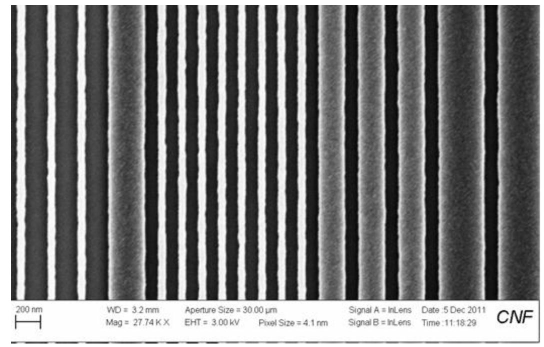
Structure and purity has been confirmed through ^{1}H and ^{19}F NMR spectra

Methyl Sweet PAG – Lithographic Characterization e-beam Patterning

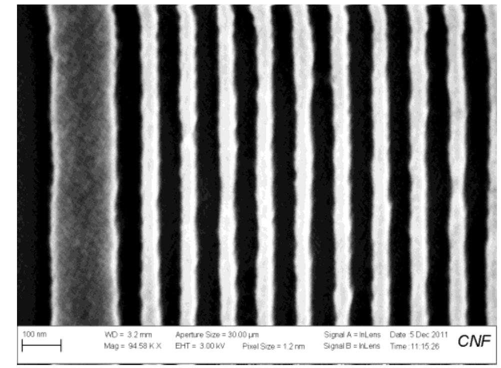


ESCAP resist with Methyl Sweet PAG

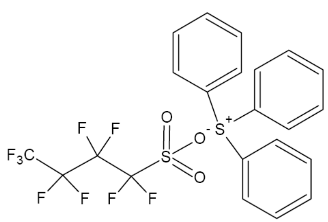
60 nm dense and isolated lines



Well-resolved 50 nm dense lines

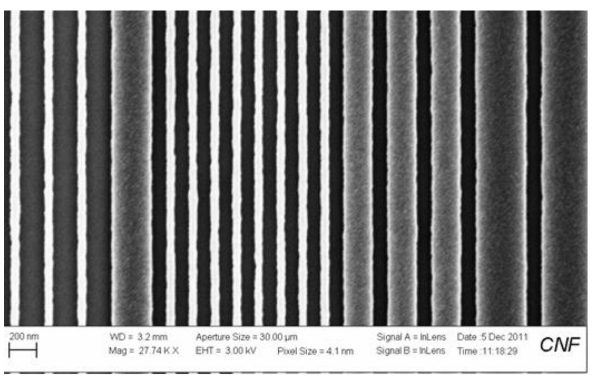


Dose = 10 μC/cm^2



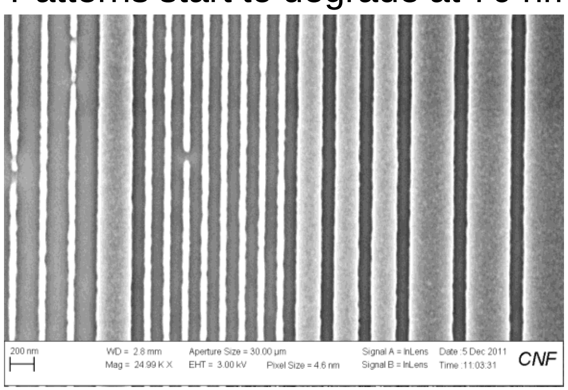
ESCAP resist with TPS-Nonaflate PAG

80 nm dense and isolated lines



70 nm dense and isolated lines

Patterns start to degrade at 70 nm



Dose = 10 μC/cm^2

Comparable sensitivity to PFOS-containing PAG

Methyl Sweet PAG outperforms PFOS-containing PAG in terms of resolution

Industrial Interactions and Technology Transfer

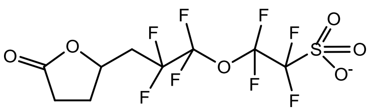
- **Collaboration with Dow Electronic Materials for photolithography tests of Sweet PAG concluded**
- **Samples provided to Orthogonal, Inc. – a small startup**
- **Performance at 193 nm and EUV evaluated with the assistance of International Sematech**
- **Ongoing interactions with Intel on LER issues**

Environmental Compatibility of New Non-PFOS PAG Anions

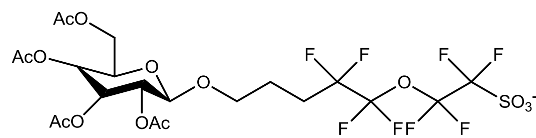
Objectives:

- Evaluate the environmental compatibility of new PAGs
- Evaluate the removal of new PAGs by biological treatment methods

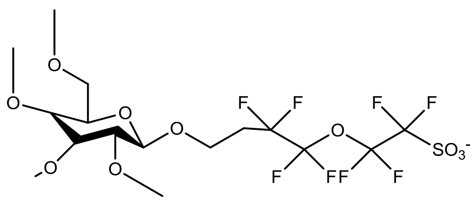
Environmental Compatibility of New Non-PFOS PAG Anions



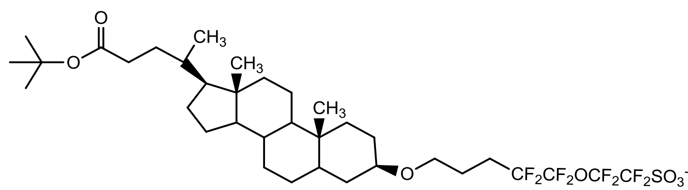
Lactone PAG



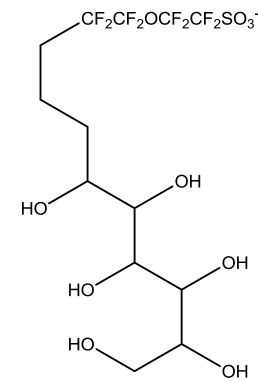
Sugar sweet PAG



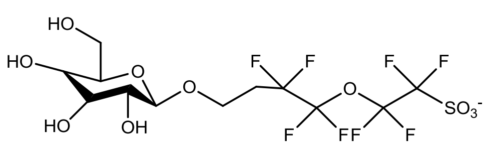
Methoxy sugar B sweet PAG



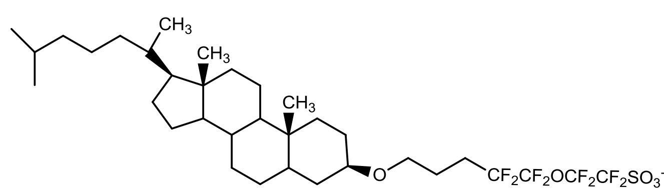
Lithocholic acid PAG



Linear sweet PAG



Hydroxy sugar B sweet PAG

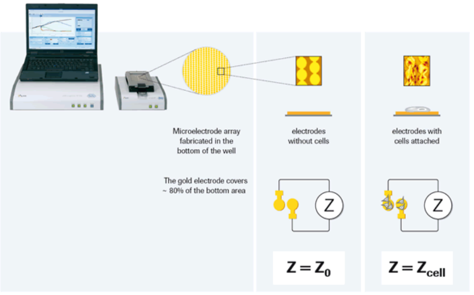


Dihydrocholesterol PAG

- 3rd Generation Non-PFOS PAGs included in the testing program

Environmental Compatibility

- **Biodegradation**
  - Batch bioassays: aerobic and anaerobic conditions
- **Toxicity**
  - Microbial inhibition (aerobic and anaerobic microorganisms)
  - Aquatic toxicity (Microtox with bacterium, *Vibrio fischeri*)
  - MTT test (mitochondrion activity)
  - Real time cell analysis or RTCA (xCELLigence)



- **Bioaccumulation**
  - K_{ow}: water-octanol partition coefficient

Microbial Degradation of New Generation PAGs

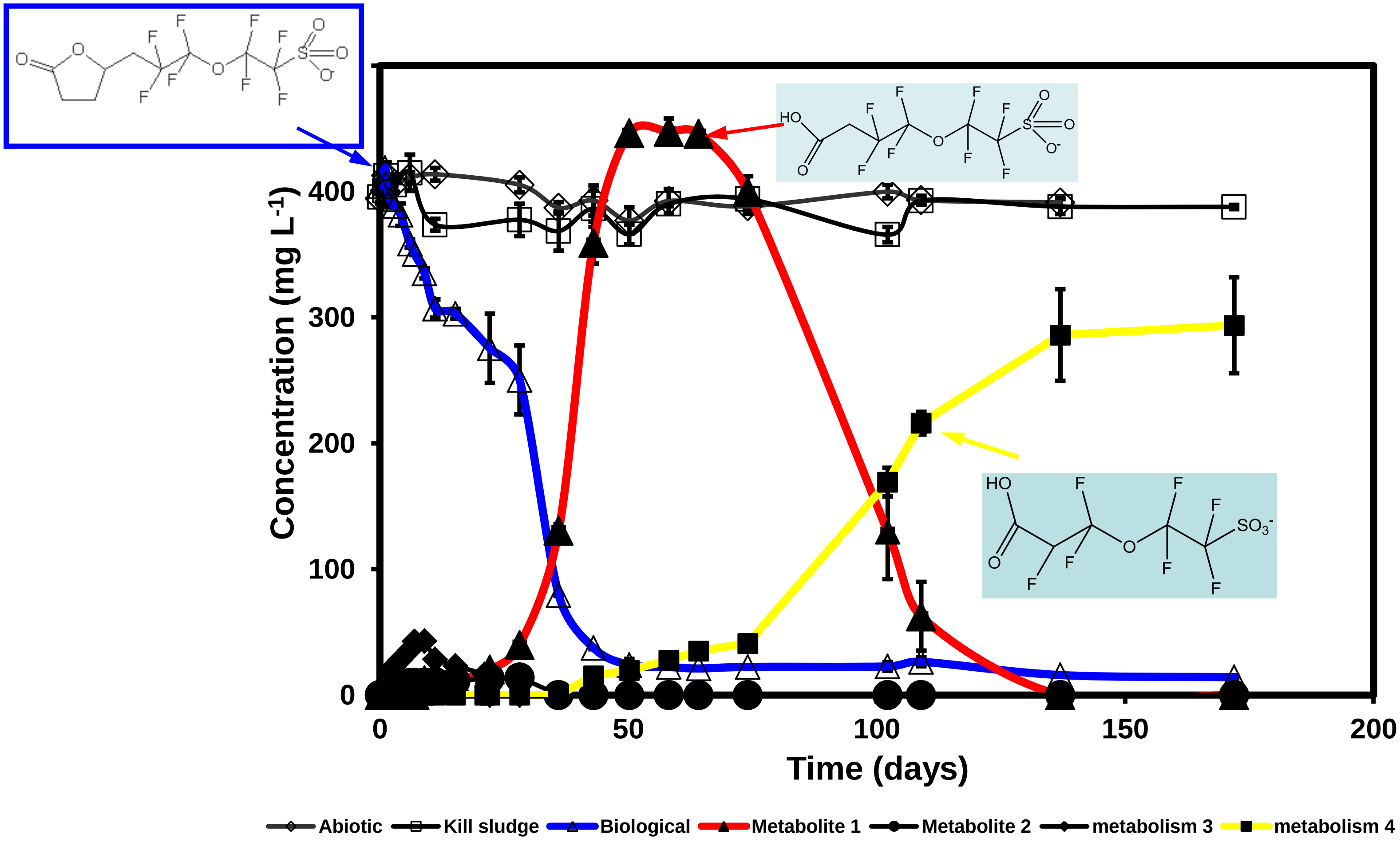
Compounds	Aerobic Degradation	Anaerobic Degradation
PFOS	NO	NO
PFBS	NO	NO
Sugar sweet PAG	YES	YES
Lactone PAG	YES	NO
Linear sweet PAG	YES	NO
Lithocholic acid PAG	YES	YES
Dihydrocholesterol PAG	YES	YES
Methoxy sweet PAG	YES	YES

Biomolecule-based PAGs are degraded by microorganisms in activated sludge.

High PAG removals anticipated in conventional wastewater treatment systems

Microbial Degradation of New Generation PAGs

Biodegradation of the "lactone PAG" by aerobic microorganisms *vs.* time

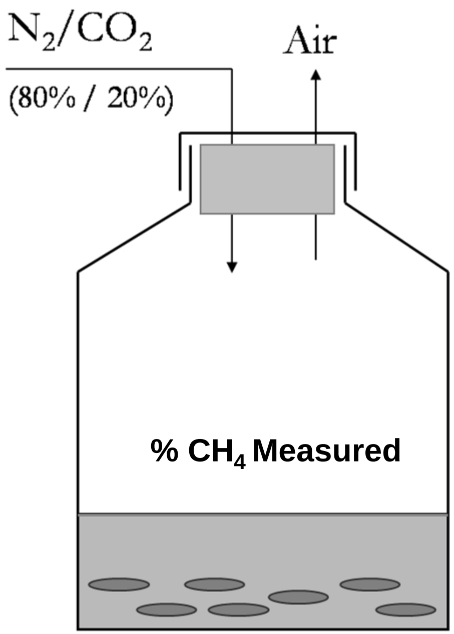


Biomolecule-based PAGs are readily degradable by aerobic bacteria in activated sludge.

SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

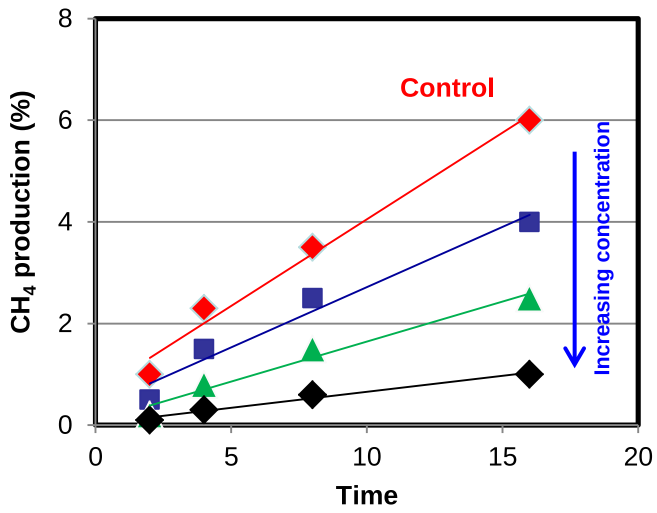
Methanogenic Inhibition of New Generation PAGs

Inhibitory effect of PAG towards methanogenic activity in anaerobic biofilms



Methanogenic Sludge

- Liquid vol.: **25** mL
- Headspace vol.: **135** mL
- Methanogenic sludge: **1.5** g VSS/L
- Mineral medium

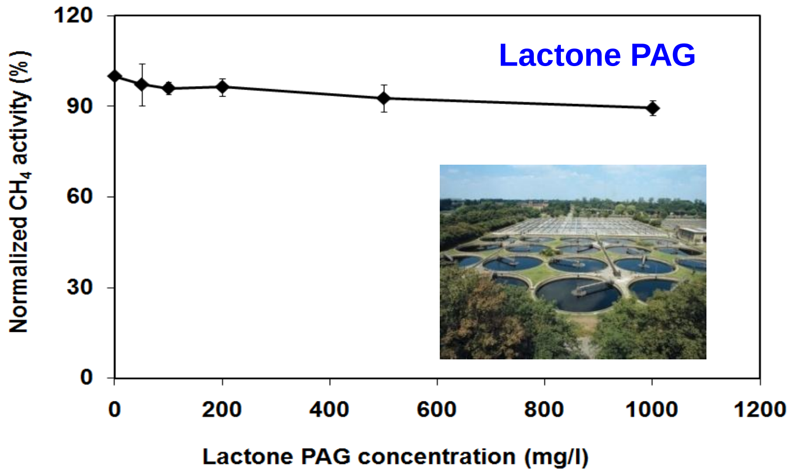


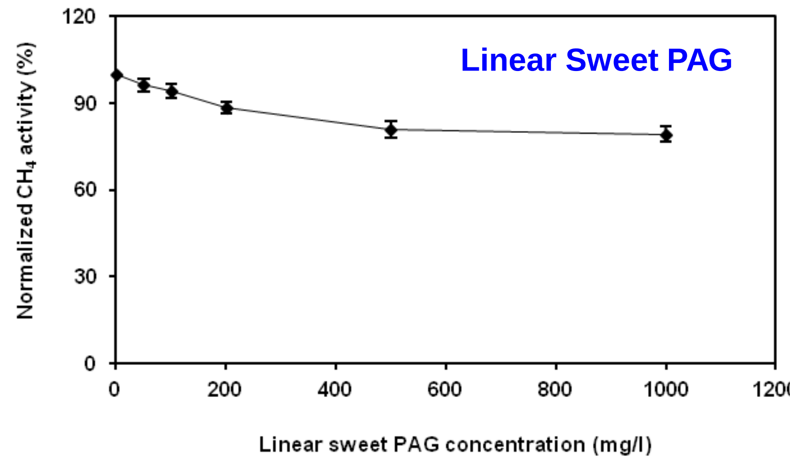
Two classes of methanogens were evaluated:

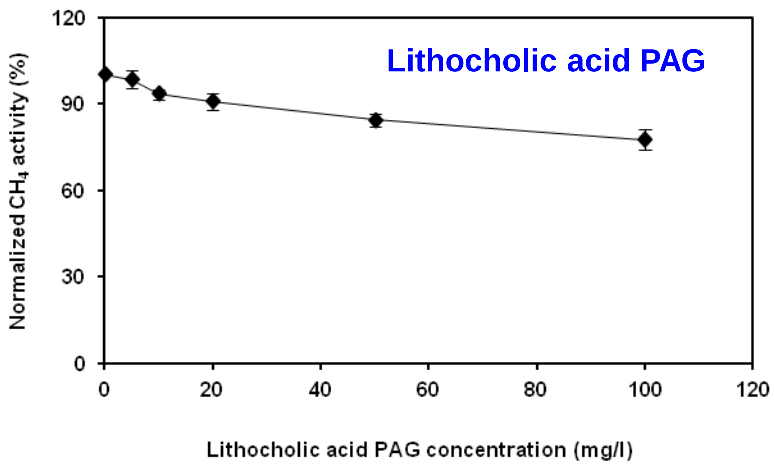
- H_2-utilizing methanogens
- Acetate-utilizing methanogens

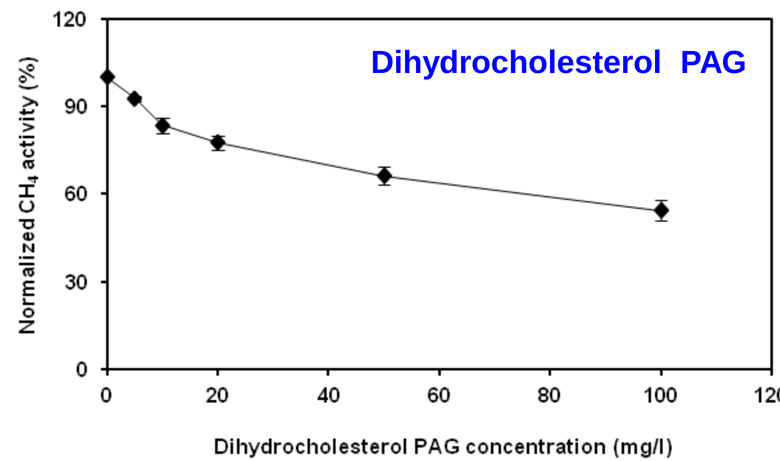
Methanogenic Inhibition of New Generation PAGs

Inhibitory effect of PAG towards methanogenic (acetoclastic) activity in anaerobic biofilms





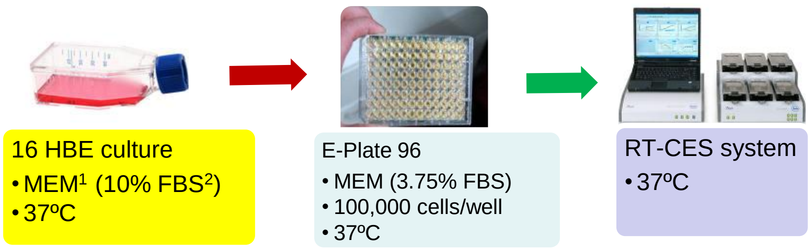


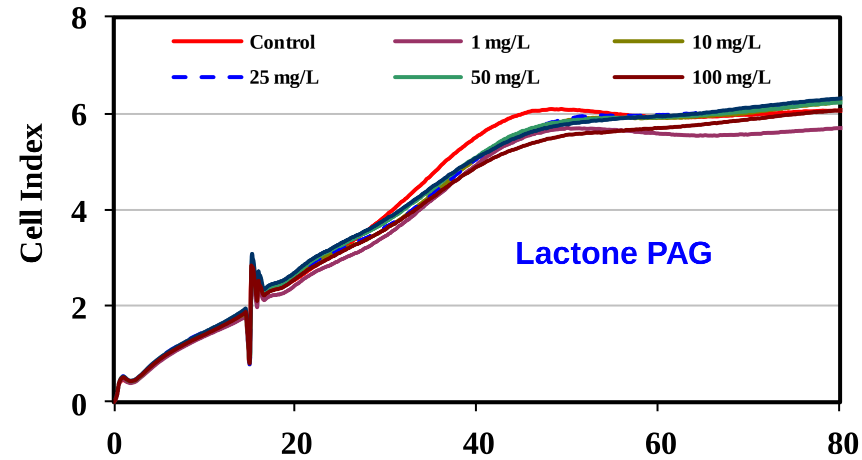


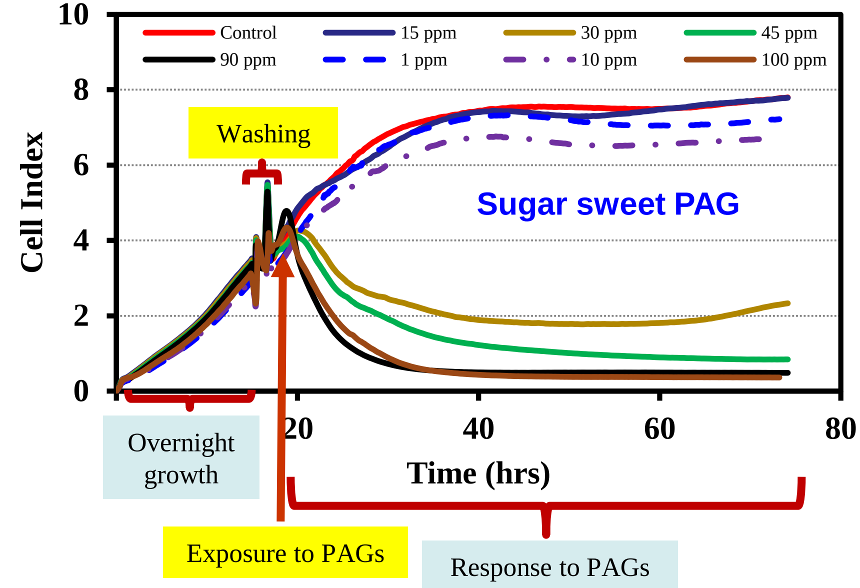
PAG compounds are not toxic to anaerobic wastewater treatment biofilms.

RTCA Cytotoxicity of New Generation PAGs

Cytotoxicity bioassay with lung epithelial 16HBE14o- cells (RTCA with xCELLigence)







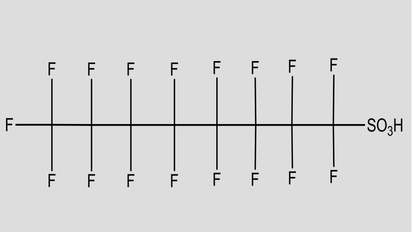
Impedance based Cell Index (CI):

Quantitative measure of the overall status of the cells:

- Cell number
- Cell adhesion and spreading
- Cell morphology

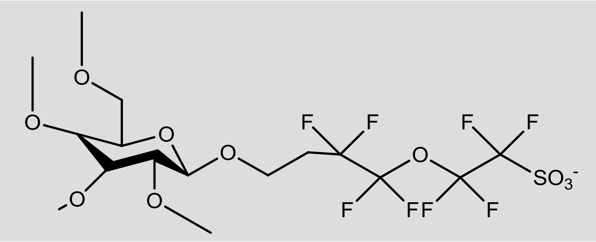
Some PAGs showed intermediate toxicity towards lung epithelial cells.

Conclusions



PFOS

(Perfluoroalkyl sulfonate)



New generation PAGs

(Biomolecule-based)

Biodegradability	NO	YES (aerobic)
Chemical degradation	NO	YES
Methanogenic toxicity	Low	Low
Cytotoxicity (human cells)	YES	+ / -- (depends on PAG)
Bioaccumulation	YES	NO

The newly developed, biomolecule-based PAGs present significant ESH advantages compared to PFOS-based PAGs.

Overall Conclusions

- **Identified PFOS free PAGS which in several cases outperformed industry standard PAGs**
- **Identified PAGs that were both biodegradable, resist compatible and environmentally friendly**
- **Sweet PAG more polar than anticipated and therefore performance not as good as other environmentally friendly PAGs**
- **The newly developed, biomolecule-based PAGs present significant ESH advantages compared to PFOS-based PAGs.**

Students on Task 425.029

- **Students and Current Affiliation**
  - Lila Otero, University of Arizona
  - Marie Krysak, Cornell University (going to Intel)
  - Nelson Felix, IBM
  - Evan Schwartz, 3M
  - Jing Sha, Intel

- **Internships (Task and related students)**
  - Marie Krysak, Intel
  - Evan Schwartz, Intel & Bayreuth
  - Anuja de Silva, IBM
  - Jing Sha, NIST

Publications, Presentations, and Recognitions/Awards

Publications

•Sun WJ, Gamez V, Field JA, Cho YJ, Ober CK, Sierra-Alvarez, R. Cytotoxicity, Biodegradability and Physico-chemical Treatability of Perfluorooctane sulfonate (PFOS)-free Photoacid Generators. (in preparation)

•Krysak M, Sun WJ, Cho YJ, Ouyang, CY, Sierra-Alvarez, R, Ober CK. Natural Occurring Biomolecules-Based Sulfonium Salts of Semifluorinated Alkyl Ether Sulfonates for Environmentally Friendly Photoacid. (in preparation)

•Cho Y., Ouyang C. Y., Sun W., Sierra-Alvarez R., Ober C. K. "Environmentally Friendly Natural Molecules Based Photoacid Generators for the Next Generation Photolithography" *Proc. SPIE,* 2011.

•Yi Y, Ayothi R, Wang Y, Li M, Barclay G, Sierra-Alvarez R, Ober CK. 2009. Sulfonium Salts of Alicyclic Group Functionalized Semifluorinated Alkyl Ether Sulfonates As Photoacid Generators" *Chem. Mater.* 2009, 21, 4037.

• Jing Sha, Byungki Jung, Michael O. Thompson, and Christopher K. Ober. 2009. Submillisecond post-exposure bake of chemically amplified resists by CO2 laser spike annealing. J. Vac. Sci. Technol. B, 27(6), 3020-3024.

• Ayothi R, Yi Y, Cao HB, Wang Y, Putna S, Ober CK. 2007. Arylonium Photoacid Generators Containing Environmentally Compatible Aryloxyperfluoroalkanesulfonate Groups" *Chem. Mater.* 2007, 19, 1434.

• Ober CK, Yi Y, Ayothi R. 2007. Photoacid generator compounds and compositions. *PCT Application* WO2007124092.

Presentations and Conference Proceedings

•Condensed Matter and Materials Physics (CMMP 10). Warwick, UK, Dec. 14-16, 2010. "Will Polymers Be Used to Make the Next Generation Nano World?", invited plenary talk.

•2010 MRS Fall Meeting, Boston, MA, November 29-December 3, 2010. "Striving for Sub-30 nm Resolution: Directed Assembly Meets Self Assembly", invited talk.

•1st RX Branch Distinguished Lecture, Air Force Research Laboratory, Dayton, OH, Nov. 1 – 5, 2010.
"The convergence of top down and bottom up patterning applied to microelectronics and the life sciences"

•2010 MRS Spring Meeting, San Francisco, CA, April 5-9, 2010. "Striving for Sub-30 nm Resolution: Using Directed or Self Assembly", invited talk.

Publications, Presentations, and Recognitions/Awards

Presentations and Conference Proceedings

•Spring 2010 ACS National Meeting, San Francisco, CA, March 21-25, 2010 “Self-assembly and directed assembly: Tools for current challenges in nanofabrication”, invited talk – Lovinger Award Symposium.

•CNF Synergies in NanoScale Manufacturing & Research Workshop, Ithaca, NY, Jan. 29, 2010. “Orthogonal Processing: A New Strategy for Patterning Organic Electronics”, invited talk.

•Sun W, Cho Y,Ober CK, Field JA, Sierra Alvarez R. 2010. Sugar-Based Photoacid Generators ("Sweet" PAGs): Environmentally Friendly Materials for Next Generation Photolithography TECHCON Conference: Technology and Talent for the 21st Century. Sept. 13-14, Austin, TX. invited talk.

•Sun W, Sierra-Alvarez R, Ober C, Cho Y. 2011. Environmentally Friendly Sugar or Natural Materials Based Photoacid Generators for Next Generation Photolithography. 2nd International Congress on Sustainability Science and Engineering. Jan. 9-14, Tucson, AZ.

•Sun WJ, Cho YJ, Sierra-Alvarez, R, Field JA, Ober CK. 2011. Environmentally Friendly Photoacid Generators for Next Generation Photolithography. The 15th Annual Green Chemistry & Engineering Conference (GC&E), joint with the 5th International Conference on Green and Sustainable Chemistry. June 21-23, Washington, DC, USA, invited talk.

•Sun WJ, Cho YJ, Field JA, Krysak M, Ober CK, Sierra-Alvarez, R. 2011. Sugar-Based Photoacid Generators (“Sweet” PAGs”): Environmentally Friendly Materials for Next Generation Photolithography. Semiconductor Research Corporation, TECHCON 2011. Sep. 11-13. Austin, TX, USA, invited talk.

Recognitions/Awards

- 2009 Gutenberg Research Awards for C. K. Ober
- 2009 Fellow of the American Chemical Society for C. K. Ober