Adsorptive Retention Performance Index for NGL Process Filters

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Introduction

Filter rating (e.g. 10 nm, 5 nm, etc.)

• Rating of a filter product is determined by

• In actual process fluids, removal is achieved by

Surfactant also minimizes adsorptive mechanisms

Sieving Adsorption
Introduction

Conceptual rendering of defect reduction performance against filter ratings.
Introduction

• Adsorption between filter media and defect sources (②) can be affected by adsorption between solvent and filter media (①) and affinity of solvent to defect sources (③).

• Therefore, adsorption effect of defect sources in filtration should be examined in each process fluid system.
Schematic Summary of the Study

Scope of current presentation

- Commercial results
  - Simulated test particle selection
    - Investigate adsorbing parameters using simulated particle
      - Establish performance index for adsorption enhanced filtration products
    - Predict appropriate filtration product for new chemical system
      - Understand adsorption mechanism
    - Filtration testing
      - Comparison
        - Search dispersible nanoparticle in process fluid
Test Particle Selection

- Test design summary

<table>
<thead>
<tr>
<th>Test fluid</th>
<th>Test filter</th>
<th>Test particle</th>
</tr>
</thead>
</table>
| Actual fluid or its solvent | Actual filter products | Defect source is usually not available  
Need to identify a test particle that exhibits adsorptive performance similar to real defects. |
Test Particle Selection

- Property of real defect source found in photoresist
  Microbridge is dominant defect on resist pattern that can be reduced using point-of-use filtration.
  Microbridge precursor adsorbs onto nylon 6,6 membrane rather than HDPE membrane.

Microbridge removal efficiency in 193 nm lithography (L/S 90 nm hp).

Test Particle Selection

- Simulation particle candidate: Metal nanoparticles
  Adsorbing property can be varied changing ligand species

Example: Pt-Decylamine (amine, C\textsubscript{10})

- Core metal nanoparticle diameter: 2 - 4 nm
  
  ![Diagram of Pt-Decylamine](image)
  
  Core metal particle which determines particle diameter
  Protective ligand which determines adsorptive property
Test Particle Selection

- Simulated particle selection in previous studies

<table>
<thead>
<tr>
<th>Base solvent</th>
<th>Cyclohexanone</th>
<th>PGMEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results</td>
<td>Pt-Decylamine showed adsorptive retention similar to microbridge pre-cursors</td>
<td>Unable to differentiate retentive performance of Pt-Decylamine in Nylon 6,6 vs. HDPE membranes</td>
</tr>
</tbody>
</table>
Test Particle Selection

- Log $P_{ow}$: Octanol-water partition coefficient
  Specific adsorption property of nylon 6,6 is assumed to be based on its hydrophilicity
  Log $P_{ow}$ describes hydrophobicity of the ligand; used to predict adsorptive property of the test particle

$$
\text{Log } P_{ow} = \text{Log} \left[ \frac{\text{solute}}{\text{solute}} \right]_{\text{octanol}} \frac{\text{un–ionized water}}{\text{solute}}
$$

Bond-line structure of nylon 6,6
Test Particle Selection

• Test nanoparticles

In the current study, removal efficiency was determined as a function of $\text{Log } P_{ow}$ of ligands.

<table>
<thead>
<tr>
<th>Core nanoparticle (4 nm)</th>
<th>Ligand</th>
<th>Log $P_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Decylamine ($C_{10}$)</td>
<td>4.1</td>
</tr>
<tr>
<td>Pd</td>
<td>Octylamine ($C_{8}$)</td>
<td>3.1</td>
</tr>
<tr>
<td>Pd</td>
<td>Heptylamine ($C_{7}$)</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Test Particle Selection

• Results

Similar microbridge removal tendency was achieved using lower-Log-P\textsubscript{ow} ligand-Pd nanoparticle.

In PGMEA, Pd-Heptylamine was found to be a good candidate particle for simulating microbridge pre-cursors.
Plan to Quantify Adsorptive Retention

• Apparent adsorption kinetics

Adsorption performance of each filter product can be quantified using apparent adsorption kinetics in the simulated filtration test system.

\[- \frac{dC}{dt} = kC^n\]

k : adsorbing rate constant
C : metal nanoparticle concentration
n : adsorbing reaction order
t : contact time
Summary

• New performance index is needed to indicate real filter performance which includes adsorptive effect.
• Substituted metal nanoparticles were found to simulate adsorptive retention of microbridge precursors.
  o Pt–Decylamine / Cyclohexanone
  o Pd–Heptylamine / PGMEA
• Adsorption performance of the filtration product to the simulation particle can be quantified using apparent adsorption kinetics.
• As a next step, rate equation constants (n, k) will be determined for various fluid systems in order to establish an adsorptive retention performance index for NGL process filters.
Appendix
Sieving Retention of 3 nm Nanoparticles

Table sieving retention of 3 nm nanoparticles in no adsorptive condition.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Nanoparticle / size</th>
<th>Solvent</th>
<th>Removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6,6 20 nm</td>
<td>Au-Hexanethiol/3 nm</td>
<td>PGMEA:PGME 95:5</td>
<td>0%</td>
</tr>
<tr>
<td>HDPE 10 nm</td>
<td>Pt-Decylamine/3 nm</td>
<td>Cyclohexanone</td>
<td>3.6%</td>
</tr>
</tbody>
</table>
Amine

Dipole moment

Metal nanoparticle

\[ \text{N} \]

\[ \text{δ}^- \]

Ligand

Thiol

Metal nanoparticle

\[ \text{S} \]

Ligand

No adsorption to HDPE

No adsorption to Nylon 6,6

High adsorption to Nylon 6,6