Alternative Green Solvents Project
Phillip Maloney

Background

- Necessary for safe and proper functioning of equipment
- Mainly halogenated solvents
  - Carbon tetrachloride
  - Trichloroethylene (TCE)
  - CFC-113
- No longer used due to regulatory/safety concerns
Precision Cleaning at KSC

- Small % of total parts
- Used for liquid oxygen (LOX) systems
- Dual solvent process
  - Vertrel MCA (decafluoropentane (DFP) and trans-dichloroethylene)
  - HFE-7100
- DFP has long term environmental concerns

Specifications and Analysis

- Highest level at KSC – 25A
- Verified by particle counting and NVR analysis

<table>
<thead>
<tr>
<th>Particulate Matter Contamination Levels</th>
<th>NVR Contamination Levels</th>
<th>Visible Contamination Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level</td>
<td>Particle Size Range (micrometers)</td>
<td>Maximum Number of Particles per 0.1 m³</td>
</tr>
<tr>
<td>-------</td>
<td>----------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>25</td>
<td>&lt;5 5 to 15 15 to 25 &gt;25</td>
<td>Unlimited*</td>
</tr>
</tbody>
</table>
Project Goals

- Identify potential replacements
  - 22 wet chemical processes
  - 3 alternative processes
- Develop test procedures
  - Contamination and cleaning
  - Analysis
- Use results to recommend alternative processes

Candidate Process Criteria

- Good solvency
- Low toxicity
- LOX compatible
- Environmentally friendly
- Low surface tension
- High vapor pressure
- Inexpensive
Processes Evaluated

<table>
<thead>
<tr>
<th>Pure Solvents</th>
<th>Proprietary Solvent Formulations</th>
<th>Alternative Technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone, ethanol, cyclohexane, ethyl acetate, isopropyl alcohol, NMP, limonene, ethyl lactate, 1-bromopropane, methyl myristate, tert-butyl acetate</td>
<td>Entron Aero, Citricolv, Inland Isoprep, Inland AV-OP-125, Inland Breakthrough, Inland Skysol, Steposol SB-W, Steposol SB-D, Steposol SC, Steposol M-8-10, Vertec Bio</td>
<td>Atmospheric plasma glow discharge (AGPD), supercritical carbon dioxide (SCCO₂), carbon dioxide snow</td>
</tr>
</tbody>
</table>

Candidate Solvents

- Easiest to integrate with existing process
- Avoided highly halogenated solvents
- Augmented with sonication, directed pressure, etc.
- May be recycled to reduce waste stream
Plasma Cleaning

- Plasma is an ionized gas (TVs, lightning, etc.)
- Created by applying electrical field to a gas
- Clean via sputtering and/or chemical reaction
- Important parameters: gas type, exposure time, energy

Supercritical CO$_2$

- Has properties of both liquid and gas
- Exists at temps $>31.1^\circ$C and pressures $>1072$ psi
- Dissolves nonpolar molecules and hydrocarbons well
- Cleaning can be enhanced by the use of cosolvents
**CO₂ Snow**

- Cleans via thermo mechanical shock or dissolution
- CO₂ density determines type of cleaning
- Technique is similar to aqueous pressure washing
- Adjustable parameters: nozzle design, velocity, additional propellants

**Solvent Testing Method**

- 2" x 2" Al coupons
- Rough and smooth textures
- Sprayed with 5 contaminants
- Rinsed with 15mL of solvent and dried for one hour or...
- Cleaned by alternative process
Analytical Methods

- Problems w/ NVR
- Gravimetric
- XPS
- Contact angle

Top 5 Solvent Results

<table>
<thead>
<tr>
<th>Solvent</th>
<th>83282</th>
<th>5606</th>
<th>Dioctyl Sebacate</th>
<th>Krytox</th>
<th>Braycote</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertrel</td>
<td>102.7</td>
<td>63.3</td>
<td>98.5</td>
<td>98.6</td>
<td>89.0</td>
</tr>
<tr>
<td>1-bromo propane</td>
<td>98.4</td>
<td>117.1</td>
<td>101.0</td>
<td>54.9</td>
<td>20.0</td>
</tr>
<tr>
<td>T-butyl acetate</td>
<td>99.1</td>
<td>102.5</td>
<td>99.3</td>
<td>54.1</td>
<td>29.2</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>93.2</td>
<td>77.8</td>
<td>95.5</td>
<td>75.6</td>
<td>33.6</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>100.4</td>
<td>79.0</td>
<td>98.8</td>
<td>66.6</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Values listed are in % cleaning efficiency determined by gravimetric analysis
Contact Angle Measurements for Alternative Technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>83282</th>
<th>Krytox</th>
<th>Braycote</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertrel MCA</td>
<td>88.7°</td>
<td>88.5°</td>
<td>96.5°</td>
</tr>
<tr>
<td>Plasma</td>
<td>44.4°</td>
<td>59.6°</td>
<td>79.3°</td>
</tr>
<tr>
<td>SCCO₂</td>
<td>&lt;10.0°</td>
<td>109.9°</td>
<td>10.0°</td>
</tr>
<tr>
<td>CO₂ Snow</td>
<td>91.5°</td>
<td>105.7°</td>
<td>108.8°</td>
</tr>
</tbody>
</table>

Values listed are in degrees as determined by contact angle measurements.

Conclusions

- No alternative matched Vertrel in this study
- No clear second place solvent
- Hydrocarbons – easy; Fluorinated greases – difficult
- Fluorinated component may be needed in replacement solvent
- Process may need to make up for shortcoming of the solvent
- Plasma and SCCO₂ warrant further testing
Continuing Efforts

- Test blends with fluorinated component.
- Further testing of plasma and SCCO₂.
- Clean complex hardware.

Continuing Efforts

- Test compatibility with soft goods.
- Round robin testing with partnering facilities.
- Scale up of technologies.
- Assess benefit to other government agencies and private partners.