Making Change Easy: Solvent Cleaning in 2019
Change in the Cleaning Industry

- Regulation – Mandatory Change
- Method
- Materials
- Process
- Test Method Change – driven by phase out
- Other: ISO / GMP
Unexpected Change

- Equipment considerations
- Safety
- Training
- Testing
- Customer considerations
- COST
What’s Changing?

• Replacement of nPB and TCE with fluorinated solvents
Trichloroethylene

TCE

Short-term and long-term exposures can potentially affect the developing fetus. High acute concentrations of TCE vapors can irritate the respiratory system and skin and induce central nervous system effects such as light-headedness, drowsiness, and headaches. Repeated (chronic) or prolonged exposure to TCE has been associated with effects in the liver, kidneys, immune system, central nervous system. EPA has concerns for effects in the developing fetus from both acute and chronic exposure. TCE is carcinogenic to people through all routes of exposure, which include inhalation, dermal (skin), and ingestion.
EPA is proposing under section 6 of the Toxic Substances Control Act (TSCA) to prohibit the manufacture (including import), processing, and distribution in commerce of TCE for use in vapor degreasing; to prohibit commercial use of TCE in vapor degreasing; to require manufacturers, processors, and distributors, except for retailers of TCE for any use, to provide downstream notification of these prohibitions throughout the supply chain; and to require limited recordkeeping.
Trichloroethylene
TCE

• Current Exposure Limits (8-hr TWA):
  OSHA: 100 ppm
  Cal/OSHA: 25 ppm
  ACGIH: 10 ppm

• HAP and TRI List
  Proposed strict regulations: Frank R. Lautenberg Act (chem of high concern)
n-Propyl Bromide

nPB, 1-bromopropane

Exposure to 1-BP can cause irritation (for example, of the eyes, mucous membranes, upper airways and skin) and can damage the nervous system. Neurologic effects can appear as headaches, dizziness, loss of consciousness, slurred speech, confusion, difficulty walking, muscle twitching, and/or loss of feeling in arms and legs [Ichihara et al. 2012]. These effects may continue among affected persons even after exposure to 1-BP has ended [Majersik et al. 2007].
n-Propyl Bromide
nPB, 1-bromopropane

• Reducing the TLV
On January 31, 2014, the ACGIH Board of Directors issued their Annual Report indicating that the NIC for 1-BP had been adopted. The 8-hour TLV-TWA for 1-BP, as determined by the ACGIH, is now 0.1 ppm.”

- US Army Public Health Command
Technical Information Paper No. 55-022-1014
n-Propyl Bromide
nPB, 1-bromopropane

- **Canada, Effective Jan 1, 2018**
  Adoption of new or revised occupational exposure limits (OELs) based on recommendations by the American Conference of Governmental Industrial Hygienists (ACGIH) to 0.1ppm.

- **Phase out – EU: June 2020**
n-Propyl Bromide
nPB, 1-bromopropane

- **Potential HAP**
  On December 28, 2016, the U.S. Environmental Protection Agency (EPA) issued a draft notice of the agency’s rationale for granting petitions to add n-propyl bromide (nPB), also known as 1-bromopropane (1-BP), to the list of hazardous air pollutants (HAP) contained in section 112(b)(1) of the Clean Air Act (CAA).
How to adopt

• Understand that we are in a changing environment
• Stay Flexible
• Review your Process
• Evaluate Equipment
• Consider Cleaning Options
Making Change Easy

- Drop-in replacements
- Improved cleaning output
- No additional training
- Improved safety profile
Making Change Easy

• Study:
  • Drop-in replacement for standard open-top degreasers
  • Side-by-side comparisons of cleaning capabilities
  • Evaluation of cleaning improvements
  • Overcoming cleaning obstacles
Type of Chemistry

• Non-flammable Solvents
• Azeotrope features
• High exposure limits
• Improved physical properties
Properties to meet your needs

• Temperature
  • Waxes, pitch, thick greases, inks, old contaminants

• Solvency
  • Polar, non-polar, hydrocarbon, aqueous

• Density
  • Particulate, ionic ingredients

• Drying rate
  • Throughput, reel-to-reel equipment, porous parts
Desirable Properties

• Low Boiling Point
  • Low enough to allow easy separation of solvent from oils, greases, other contaminants via simple distillation

• Low Latent Heat
  • Provides increased mass of vapor per unit of heat input, reducing the cost of vaporizing the solvent
Desirable Properties

- Rapid boiling/drying decreases energy costs
  - Reduces drag out losses
- High Vapor Density
  - Allows increased solvent vapor recovery
  - Reduces solvent losses through work transfer and air disturbance of vapor blanket
## Solvent Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>TCE</th>
<th>nPB</th>
<th>Opteon SF79</th>
<th>Vertrel SDG</th>
<th>Novec 72DA</th>
<th>Novec 72DE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kb</td>
<td>129</td>
<td>90</td>
<td>100</td>
<td>95</td>
<td>58</td>
<td>52</td>
</tr>
<tr>
<td>GWP</td>
<td>0</td>
<td>0</td>
<td>&lt;1</td>
<td>148</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>Boiling Point °C</td>
<td>87</td>
<td>71</td>
<td>47</td>
<td>43</td>
<td>44</td>
<td>43</td>
</tr>
<tr>
<td>Vapor Pressure mmHg</td>
<td>60</td>
<td>150</td>
<td>331</td>
<td>388</td>
<td>360</td>
<td>350</td>
</tr>
<tr>
<td>Liquid density g/mL</td>
<td>1.46</td>
<td>1.35</td>
<td>1.28</td>
<td>1.29</td>
<td>1.27</td>
<td>1.28</td>
</tr>
<tr>
<td>Surface tension dynes/cm</td>
<td>29.5</td>
<td>25.9</td>
<td>21</td>
<td>21.2</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>Exposure limit 8-hr TWA (ppm)</td>
<td>10</td>
<td>1</td>
<td>200</td>
<td>193</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>
Case Studies

- Coolants
- Greases
- Oil Lubricants
- Waxes and Pitch
- Rust Inhibitors
Coolants

- Solvency is key
  - High Kb value
  - Polar v non-polar components
- Hydrocarbon v. aqueous-based
- No changes in cleaning time
- Similar throughput
### Solubility limitations

#### Gravimetric Data: Cleaning with nPB

<table>
<thead>
<tr>
<th>Mass of Clean Part</th>
<th>Mass of Soiled Part</th>
<th>Mass after cleaning</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.64</td>
<td>48.88</td>
<td>48.62</td>
<td>0.02</td>
</tr>
<tr>
<td>37.83</td>
<td>37.91</td>
<td>37.84</td>
<td>0.01</td>
</tr>
<tr>
<td>1.30</td>
<td>1.34</td>
<td>1.31</td>
<td>0.01</td>
</tr>
<tr>
<td>10.50</td>
<td>10.55</td>
<td>10.50</td>
<td>0.00</td>
</tr>
</tbody>
</table>

#### Gravimetric Data: Cleaning with Fluorinated

<table>
<thead>
<tr>
<th>Mass of Clean Part</th>
<th>Mass of Soiled Part</th>
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<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.86</td>
<td>49.17</td>
<td>48.89</td>
<td>0.03</td>
</tr>
<tr>
<td>37.83</td>
<td>38.26</td>
<td>37.83</td>
<td>0.00</td>
</tr>
<tr>
<td>1.30</td>
<td>1.42</td>
<td>1.30</td>
<td>0.00</td>
</tr>
<tr>
<td>10.51</td>
<td>10.54</td>
<td>10.50</td>
<td>0.01</td>
</tr>
</tbody>
</table>

nPB on left. Opteon SF79 on right.
Solubility limitations

<table>
<thead>
<tr>
<th></th>
<th>Mass of Clean Part</th>
<th>Mass of Soiled Part</th>
<th>Mass after cleaning</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Data: Cleaning with TCE</td>
<td>48.86</td>
<td>49.08</td>
<td>48.88</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>37.84</td>
<td>38.05</td>
<td>37.83</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>1.34</td>
<td>1.30</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>10.50</td>
<td>10.54</td>
<td>10.50</td>
<td>0.00</td>
</tr>
</tbody>
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</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Data: Cleaning with Fluorinated</td>
<td>48.88</td>
<td>49.25</td>
<td>48.86</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>37.83</td>
<td>38.29</td>
<td>37.84</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>1.39</td>
<td>1.31</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>10.50</td>
<td>10.62</td>
<td>10.51</td>
<td>0.01</td>
</tr>
</tbody>
</table>

TCE on left. Tergo MCF on right.
Coolants: Solubility limitations

• Solubility limitations may impact cleaning due to lower boiling point.

• High density and low surface tension help to overcome solubility obstacles.

• Equal/better cleaning results are possible with the aid of solvent manipulation (ultrasonic cavitation, immersion spray, vapor spray)
Greases

• Solvency is key
  • Must be able to cut through without aid of heat
• Low surface tension
  • Penetrate between tight tolerances
• Organic and inorganic ingredients
## Temperature limitations

### Gravimetric Data: Grease Removal in nPB

<table>
<thead>
<tr>
<th>Part Number</th>
<th>Mass before Cleaning (g)</th>
<th>Mass with Grease (g)</th>
<th>Mass After Cleaning (g)</th>
<th>Grease removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16-037031</td>
<td>740.07</td>
<td>742.24</td>
<td>740.20</td>
<td>94%</td>
</tr>
<tr>
<td>13-101757</td>
<td>740.20</td>
<td>743.60</td>
<td>740.19</td>
<td>100%</td>
</tr>
<tr>
<td>15-63883</td>
<td>740.19</td>
<td>742.01</td>
<td>740.18</td>
<td>100%</td>
</tr>
</tbody>
</table>

### Gravimetric Data: Grease Removal in Fluorinated

<table>
<thead>
<tr>
<th>Part Number</th>
<th>Mass before Cleaning (g)</th>
<th>Mass with Grease (g)</th>
<th>Mass After Cleaning (g)</th>
<th>Grease removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14-67636</td>
<td>740.18</td>
<td>742.58</td>
<td>740.16</td>
<td>100%</td>
</tr>
<tr>
<td>14-67635</td>
<td>740.16</td>
<td>742.63</td>
<td>740.13</td>
<td>100%</td>
</tr>
<tr>
<td>10-63538</td>
<td>740.13</td>
<td>744.23</td>
<td>740.13</td>
<td>100%</td>
</tr>
</tbody>
</table>
Greases: Temperature limitations

- Temperature differences are offset by improved solvency
  - nPB boiling point: 71 °C
  - nPB Kb value: 90
  - Fluorinated boiling point: 47 °C
  - Fluorinated Kb: 100
- Low surface tension improves cleaning in tight tolerances
Oil Lubricants

- Typically organic composition
- Require fast drying
  - Reel-to-reel equipment
  - High throughput
  - Multiple cleanings
## Gravimetric Data: Multiple Cleanings with Fluorinated Cleaner

<table>
<thead>
<tr>
<th>Part ID</th>
<th>Initial Weight (g)</th>
<th>Weight after 1st Cleaning (g)</th>
<th>Weight after 2nd Cleaning (g)</th>
<th>Total Mass Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>23.0030</td>
<td>23.0013</td>
<td>23.0014</td>
<td>0.0004</td>
</tr>
<tr>
<td>#2</td>
<td>46.2452</td>
<td>46.2397</td>
<td>46.2382</td>
<td>0.0032</td>
</tr>
<tr>
<td>#3</td>
<td>18.4806</td>
<td>18.4735</td>
<td>18.4734</td>
<td>0.0005</td>
</tr>
<tr>
<td>#4</td>
<td>68.5662</td>
<td>68.5488</td>
<td>68.5487</td>
<td>0.0001</td>
</tr>
</tbody>
</table>
Oil Lubricants

- Easy transition from legacy solvents to fluorinated solvents
- Solvency and physical properties do not impact cleaning time/rate
- Drying time equal or faster than prior solvent
- Equipment modifications for temperature may be required
Waxes and Pitch

• Thick contamination
• Typically requires high heat
• Particle removal
• Organic composition
## Wax Solubility

### Heated Solubility Evaluation

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Volume (mL)</th>
<th>Mass (g)</th>
<th>Total PEG Added (g)</th>
<th>Percent PEG @ saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>nPB</td>
<td>98</td>
<td>130</td>
<td>35</td>
<td>27%</td>
</tr>
<tr>
<td>Fluorinated</td>
<td>99</td>
<td>127</td>
<td>60</td>
<td>47%</td>
</tr>
</tbody>
</table>

### 25 °C Solubility Evaluation

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Volume (mL)</th>
<th>Mass (g)</th>
<th>Total PEG Added (g)</th>
<th>Percent PEG @ saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>nPB</td>
<td>100</td>
<td>132</td>
<td>1</td>
<td>1%</td>
</tr>
<tr>
<td>Fluorinated</td>
<td>103</td>
<td>131</td>
<td>50</td>
<td>38%</td>
</tr>
</tbody>
</table>
Wax Solubility

- High solvency aids in wax dissolution with low temperatures
- Soil-loading is greater than legacy solvents
- Less energy required
Wax Extraction

- Wax extraction equal to nPB
- Low surface tension and high \(K_b\) allow for good penetration
- Chemical stability with metals improves cleaning process
Wax Extraction: Drying Time

- Fluorinated solvents show faster drying time
- High vapor pressure, low boiling point, low surface tension

Drying Evaluation at Room Temperature

25 °C

- nPB 1
- nPB 2
- MCF 1
- MCF 2
Waxes

• Improved cleaning processes
  • Faster cleaning
  • Faster wax extraction
  • Better soil-loading
  • Faster drying

• Solvency allows for processing at lower temperatures
  • Better for temperature-sensitive parts
  • Energy efficiency
Rust Inhibitors

• Organic composition
• Particulate and metal fines
• Compatibility
  • Cannot contain/attract water
# Rust Inhibitors

## Gravimetric Data: Parts Cleaned in nPB

<table>
<thead>
<tr>
<th>Mass of Clean (g)</th>
<th>Mass in Oil (g)</th>
<th>Mass Post Cleaning (g)</th>
<th>Oil Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.7888</td>
<td>54.2712</td>
<td>53.7888</td>
<td>100%</td>
</tr>
<tr>
<td>53.7888</td>
<td>53.8979</td>
<td>53.7885</td>
<td>100%</td>
</tr>
<tr>
<td>53.7885</td>
<td>53.9981</td>
<td>53.7887</td>
<td>100%</td>
</tr>
</tbody>
</table>

## Gravimetric Data: Parts Cleaned in nPB

<table>
<thead>
<tr>
<th>Mass of Clean (g)</th>
<th>Mass in Oil (g)</th>
<th>Mass Post Cleaning (g)</th>
<th>Oil Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.8110</td>
<td>54.1212</td>
<td>53.8111</td>
<td>100%</td>
</tr>
<tr>
<td>53.8112</td>
<td>54.1916</td>
<td>53.8109</td>
<td>100%</td>
</tr>
<tr>
<td>53.8110</td>
<td>54.1108</td>
<td>53.8110</td>
<td>100%</td>
</tr>
</tbody>
</table>
Rust Inhibitors

• Similar to oil lubricant cleaning
• Easy transition from legacy solvents to fluorinated solvents
• Drying time equal or faster than prior solvent
• Equipment modifications for temperature may be required
• Fluorinated solvent has low water miscibility to prevent oxidation/corrosion
• Fluorinated solvent is stable and does not form acidic conditions
Conclusions
Conclusions

- A specific mixture of solvents having a constant boiling Pt.
- Low surface tension
- Good solvency
- Non-flammable
- Compatible with existing equipment designs
- Thermally and Hydrolytically stable
- Consistent performance and safety
Conclusions

• Cleaning consistent with nPB and TCE in all cases
• Cleaning times and equipment remain unchanged
• No additional training
• Wax extraction improved with fluorinated solvents due to high solvency and fast evaporation
• Soil loading increased in fluorinated solvents with some contaminants (wax and PEG)
• Change doesn’t need to be difficult.
Thank you

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