Laboratory Evaluation of Drop-in Solvent Alternatives to n-Propyl Bromide for Vapor Degreasing

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Acknowledgements

• This study was performed for the U.S. Army Research Laboratory
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• Alternative solvents for these tests were supplied by:
  – 3M
  – DuPont Fluoroproducts
  – AGC Chemicals Americas, Inc.
Ground rules for this study

- Test solvent effectiveness in the vapor phase only
  - Effectiveness using spray, immersion, ultrasound, etc. were not evaluated in this study
- Alternative solvent candidates must:
  - Have lower expected toxicity than nPB
  - Not be a Hazardous Air Pollutant (HAP)
  - Not be an Ozone Depleting Substance (ODS)
  - Have no flash point
  - Be compatible with existing vapor degreasers
Solvents Tested

- Ensolv® n-Propyl Bromide (baseline)
- Alternative solvents tested were all azeotropes or azeotrope-like blends of trans-1,2 dichloroethylene with other solvents.
  - tDCE is an effective solvent on greases and oils but is too flammable for use in vapor degreasers
  - Non-flammable solvents are blended with tDCE to suppress flammability while maintaining solvency
  - Blending may also lower VOC content, GWP and cost, and improve exposure limits.

Ensolv® Enviro Tech International, Inc.
Alternative Solvents Tested:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling Point</th>
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<tbody>
<tr>
<td>Novec™ HFE 72DE (3M)</td>
<td>113°F</td>
</tr>
<tr>
<td>Vertrel® SDG (DuPont)</td>
<td>109°F</td>
</tr>
<tr>
<td>Azeotrope A1 R&amp;D Solvent (DuPont)*</td>
<td>118°F</td>
</tr>
<tr>
<td>AE3000ATE (Asahi Glass Co., Ltd)*</td>
<td>108°F</td>
</tr>
<tr>
<td></td>
<td>(nPb 156°F)</td>
</tr>
</tbody>
</table>

*These solvents are not yet approved by the EPA for use in the United States. Samples were provided by the suppliers “for laboratory use only”.

Note: Perfluorobutyl iodide was to be included in this study but a suitable sample was not available in the required time frame.
What is an Azeotrope?

- A mixture of two or more liquids at a ratio where, when boiled, the resulting vapor has the same composition as the liquid.
- This lends stability to maintain the properties of the blend over time, critical in vapor degreasing applications.
Materials Compatibility Tests

- Test coupons were immersed in boiling solvent for 30 minutes; observed and weighed before & after
- Materials Tested:
  - Aluminum 7075-T6
  - Magnesium AZ31B-H24
  - Steel Maraging C-250
- No degradation was observed with any of the solvents.
Cleaning Effectiveness Tests

- A standard contaminant was applied to aluminum 2219 coupons and baked for 2 hours at 130°F.
- All coupons were photographed and weighed:
  - Before contamination
  - After contamination and baking
  - After vapor degreasing for 30 minutes
- Photos were taken in bright white and long wave ultraviolet light
- Clean control coupons, degreased and not degreased, were included.
Standard Contaminant per ADS-61A-PRF*

Mixed, brushed on, and baked two hours at 130°F:

2 parts* MIL-PRF-83282
   Fire resistant, synthetic hydrocarbon base hydraulic fluid

1 part* MIL-PRF-81322
   General purpose aircraft grease

1 tenth* part Carbon Black

*by weight

*ADS-61-PRF Performance Specification, Cleaners, Aqueous and Solvent, For Army Aircraft
Contaminant applied to test coupons

Aluminum 2219 sheet – 2.5 in. x 6 in.
Cleaning Results – Set 1

Smooth coupon surface, contaminant removed same day as applied
(Typical visual appearance and average percent removal)

- **Ensolv nPB**: 98.2% removed
- **Novec HFE 72DE**: 97.3% removed
- **Vertrel SDG**: 99.4% removed
- **Azeo A1**: 99.2% removed
- **AE3000ATE**: 99.2% removed
Cleaning Results under UV – Set 1

Smooth coupon surface, contaminant removed same day as applied (Typical appearance under UV and average percent removal)
Cleaning Results – Set 1

Three solvents show very similar results.
Cleaning Results – Set 2, aged contaminant

Smooth coupon surface, contaminant removed 7 days after application
(Typical visual appearance and average percent removal)
Cleaning Results – Set 2, aged contaminant

Smooth coupon surface, contaminant removed 7 days after application
(Typical appearance under UV and average percent removal)
Cleaning Results – Set 2, aged contaminant
Cleaning Results – Set 3, rough surface

Grit blasted coupon surface, contaminant removed same day as applied
(Typical visual appearance and average percent removal)
Cleaning Results – Set 3, rough surface

Grit blasted coupon surface, contaminant removed same day as applied
(Typical appearance under UV and average percent removal)

- Ensolv nPB 97.7% removed
- Novec HFE 72DE 99.7% removed
- Vertrel SDG 99.4% removed
- Azeo A1 99.5% removed
- AE3000ATE 98.5% removed
Cleaning Results – Set 3, rough surface

Cleaning Effectiveness Ranges and Averages Set 3

Cleaning efficiency

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Cleaning efficiency</th>
</tr>
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<tbody>
<tr>
<td>Ensolv nPB</td>
<td></td>
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<tr>
<td>Novec HFE 72DE</td>
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<td>Azeo A1</td>
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<tr>
<td>AE3000 ATE</td>
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</table>
Combined Cleaning Results

Cleaning Effectiveness Ranges and Averages - Combined

Solvent

Cleaning Efficiency

94.0 95.0 96.0 97.0 98.0 99.0 100.0
Cleaning effectiveness versus tDCE content

* tDCE% as shown in the Vendor Technical Data Sheet
** tDCE% as shown in the Material Safety Data Sheet
Results

• All solvents were compatible with metals tested
• All solvents cleaned in the range of or better than n-propyl bromide
  – Vertrel SDG cleaned the most consistently; AE3000ATE was very close.
  – All but Vertrel SDG showed reduced cleaning effectiveness on aged contamination
  – Cleaning effectiveness did NOT correlate with tDCE%
  – Cleaning effectiveness of any of these solvents may be adequate for the end use
• Results may vary with other materials, contaminants, and hardware configurations
Observations about the test method

- Both carbon black and ultraviolet light were useful visual indicators of contaminant residues.
- Despite the two-hour bake, contaminant aged just a few days was more difficult for some solvents to remove.
- Results varied between smooth and roughened test coupons.
- Contaminant aging had a more significant impact on cleaning effectiveness than surface roughening.
Conclusions

- Based on this limited laboratory study, solvent blends of trans-1,2 dichloroethylene with HFEs, HFCs, or PFCs appear to be viable alternatives to n-propyl bromide for vapor degreasing.
  - The lower boiling points of these blends may lead to greater solvent loss during use.
  - Additional factors must be considered when selecting a solvent substitute, including stability over time, VOC, GWP, toxicity, and business considerations.
Questions?

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