Green Chemistry and the Search for New Plasticizers

International Symposium on Alternatives Assessment
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Sustainability? Green Chemistry?
Why is it important to measure or quantify?

- Informed substitution
  - Know what you are getting
  - Ensure that you are making an improvement

- Avoid regrettable substitution
  - Avoid the need for reformulation later
  - Reduce the risk of future regulatory issues

- Responsible approach to ingredient/product selection
Plasticizer Examples:
DEHP, DOTP, D9CH

Di-2-ethylhexyl phthalate (DEHP or DOP)
Or other alcohols: isononyl (DINP),
isodecyl (DIDP), propylheptyl (DPHP),
linear alcohols

Di-2-ethylhexyl terephthalate (DOTP/DEHT):
BASF Palatinol® DOTP, Eastman 168™

Di-isounonyl cyclohexane-1,2-dicarboxylate (D9CH):
BASF Hexamoll® DINCH®
Plasticizer applicability

- Ortho-phthalates
  - Low molecular weight (C8)
  - High molecular weight (C9/C10)
- Adipates
- Citrates
- Benzoates
- Trimellitates (TOTM)
- Terephthalates (DOTP)
- 1,2-Cyclohexanedicarboxylates (D9CH)
- Polymeric
- Specialty
- General purpose
# Performance Data

## Plasticizer Performance Summary

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Cost</th>
<th>Efficiency</th>
<th>Low Temp.</th>
<th>Processing</th>
<th>UL Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEHP</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>DIDP</td>
<td>9</td>
<td>7</td>
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<tr>
<td>DUP</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>3</td>
<td>9</td>
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<tr>
<td>TOTM</td>
<td>7</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>10</td>
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<tr>
<td>DINP</td>
<td>10</td>
<td>9</td>
<td>7</td>
<td>8</td>
<td>5</td>
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<tr>
<td>DOTP</td>
<td>10</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>DPHP</td>
<td>9</td>
<td>7</td>
<td>6</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>L911P</td>
<td>5</td>
<td>8</td>
<td>10</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>

**DEHP**: Di-2-ethylhexyl phthalate (C8)  
**DOTP**: Di-2-ethylhexyl terephthalate (C8)  
**DINP**: Di-isononyl phthalate (branched C9)  
**L911P**: Linear nonyl, undecyl phthalate (C9,10,11)  
**DIDP**: Di-isodecyl phthalate (branched C10)  
**DUP**: Diundecyl phthalate (linear C11)  
**DPHP**: Dipropylheptyl phthalate (C10)  
**TOTM**: Tri-2-ethyhexyl trimellitate
Hazard Assessment: GreenScreen® for Safer Chemicals

- Tool developed by Clean Production Action (CPA)
  - Publically available, transparent methodology
  - Self-assessed or external 3rd party – “certified” or “verified”
  - **Full set of endpoints, minimum data requirements** for each Benchmark
    - Studies on product under review and/or suitable modelling or surrogate data
    - **Data gaps not “rewarded”**
    - List translator (LT) or full GreenScreen assessment
    - GHS criteria, “authoritative” (SVHC, Prop 65) and “screening” lists
  - Some end points are **subjective** (e.g., endocrine activity) and open to discussion
  - **Hazard** is only one part of an effective alternatives assessment process
How might it work (BASF and/or 3rd party assessments)

| GreenScreen® - Hazard Ratings: DEHP;  
<table>
<thead>
<tr>
<th>Di-(2-ethylhexyl) phthalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human toxicity</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>M/H</td>
</tr>
</tbody>
</table>

**Benchmark 1**
Cancer: Prop 65, but IARC 2B: Possibly carcinogenic to humans
Reproductive, Developmental: EU Cat 1B, REACH SVHC

*Endocrine: positive anti-androgenic (EPA - Furr et al, 2014, and other Studies showing ED effects)*

| GreenScreen® - Hazard Ratings:  
<table>
<thead>
<tr>
<th>Alternative 1</th>
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<tbody>
<tr>
<td>Human toxicity</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>dg</td>
</tr>
</tbody>
</table>

**Benchmark U**
What about bio? What about FDA clearance?

### GreenScreen® - Hazard Ratings: Bio 1

<table>
<thead>
<tr>
<th>Human toxicity</th>
<th>Ecotox</th>
<th>Fate</th>
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<tbody>
<tr>
<td>C M R D E AT RD N SnS SnR IrS IrE AA CA P B</td>
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<td>dg L L L dg L L L L L L L L vL M</td>
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**Benchmark U**

### GreenScreen® - Hazard Ratings: Bio 2

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<th>Ecotox</th>
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<tr>
<td>dg L dg L dg L L dg L dg L dg L L vL L</td>
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</tr>
</tbody>
</table>

**Benchmark U**

### GreenScreen® - Hazard Ratings: Bio 3

<table>
<thead>
<tr>
<th>Human toxicity</th>
<th>Ecotox</th>
<th>Fate</th>
</tr>
</thead>
<tbody>
<tr>
<td>C M R D E AT ST N SnS SnR IrS IrE AA CA P B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dg L L dg dg L L dg L dg L L L L vL L</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Benchmark U**
Di-2-ethylhexyl terephthalate (Palatinol® DOTP)

GreenScreen Benchmark Score and Hazard Summary Table: DEHT (6422-86-2) was assigned a Benchmark Score of 3DG.

<table>
<thead>
<tr>
<th>GreenScreen™ Hazard Ratings: Bis(2-ethylhexyl) terephthalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I Human</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>L</td>
</tr>
</tbody>
</table>

Data gap?
- No anti-androgenic effects
- No estrogenic effects, in vivo or in vitro
- Inactive in EPA ToxCast and EDSP 21 assays
- No thyroid or adrenal gland effects in subchronic and chronic studies
D9CH (Hexamoll® DINCH®)

Benchmark 2

Endocrine activity?
- Rodent thyroid effects due to indirect mechanism and not relevant to humans (NICNAS, EFSA, NSF International)
- Negative in EPA fetal testosterone screen
- Inactive in EPA ToxCast and EDSP21 assays
- ANSES (under REACH RMOA) – no risk management required
Summary

- Beware of sustainability or health and safety claims based on labels
- Demand data to support the safe use and sustainability of products
  - Show me the data!
- Tools and certification methodologies are available to help
  - Consider using them to support your own and your customers’ initiatives
  - EPA SaferChoice and CleanGredients
- The data available for alternative plasticizers vary from product to product
  - Practice “informed substitution”
  - Avoid “regrettable substitution”

See, Harmon and Otter, ACS Sustainable Chem Eng, 2018, 6, 2078-2085.
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