Improvements in Stick Deodorants and Roll-On Antiperspirants using Zemea® Propanediol

Performance is in our nature.

April 21, 2016  Denis Burlaud, Account Executive
Agenda

• Company Overview
• Zemea® Propanediol Overview
• Introduction
• Formulating Clear, Natural Deodorant Sticks
• Formulating Conventional and Clear Antiperspirant Roll-Ons
• Conclusion
Company Overview
Company
Joint venture formed in 2004 between DuPont and Tate & Lyle to produce biobased propanediol from fermentation of glucose.

DuPont is a world leader in science and innovation across a range of disciplines, including agriculture and industrial biotechnology, chemistry, biology, materials science and manufacturing. CY2015 revenues were $35 billion.

Tate and Lyle is a global provider of renewable ingredients, solutions and services to the food, beverage and industrial customers. Revenues were $4.3 billion for Fiscal Year ending March 31, 2015.
Production

Loudon, Tennessee – USA

Production

• Started November 2006
• Capacity expanded 35% in 2010
• Current Capacity = 63 KT/year.
• Purity : 99.99%
• 100% sustainably and renewably sourced
Zemea® Propanediol Overview
Zemea® Benefits in Your Personal Care Formulations

• Unique solubility properties
• No skin irritation or sensitization
• Excellent moisturizing effects
• Boosts efficacy of preservatives
• Improves sensorial attributes
• Environmentally Sustainable
• 100% Natural, Petroleum-free
No Skin Irritation Observed with Zemea® Propanediol

Human Skin Patch Test Results
(207 individuals exposed to Zemea® propanediol or Propylene Glycol or Control at 7pH)

Irritation Response, %
(clinically significant dermal irritation)

<table>
<thead>
<tr>
<th>Concentration Level</th>
<th>Zemea® Propanediol</th>
<th>Propylene Glycol</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>50%</td>
<td></td>
<td>21.7%</td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td></td>
<td>22.7%</td>
<td>0%</td>
</tr>
</tbody>
</table>

At concentrations as high as 75%, Zemea® propanediol did not produce skin irritation or sensitization reactions.
Enhanced Skin Moisturization with Zemea® Propanediol

Averages (normalized to baseline)

Time, in hours

Zemea® Propanediol
Butylene Glycol
Propylene Glycol
Control
## Zemea® Propanediol Boosts Preservative Efficacy

<table>
<thead>
<tr>
<th>Preservative, Weight %</th>
<th>Staphylococcus aureus</th>
<th>Escherichia coli</th>
<th>Pseudomonas aeruginosa</th>
<th>Candida albicans</th>
<th>Aspergillus niger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcare PM3 (0.15%)</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>euxyl® PE 9010 (0.25%)</td>
<td>4%</td>
<td>4%</td>
<td>2%</td>
<td>6%</td>
<td>2% (1 Log reduction)</td>
</tr>
<tr>
<td>Neolone PE (0.3%)</td>
<td>2%</td>
<td>2%</td>
<td></td>
<td>6%</td>
<td></td>
</tr>
<tr>
<td>Jecide CAP-4 Optiphen (0.25%)</td>
<td>2%</td>
<td>2%</td>
<td></td>
<td>6%</td>
<td></td>
</tr>
<tr>
<td>Lexgard® Natural (0.5%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dermosoft 688 ECO (0.1%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geogard® ULTRA (0.5%)</td>
<td></td>
<td></td>
<td></td>
<td>2%</td>
<td></td>
</tr>
</tbody>
</table>

Preservative levels provided sufficient reduction to <1.00 CFU/g without addition of Zemea® propanediol

### Organisms Reduced to <1.00 CFU/g at Day 7

Minimum percentage of Zemea® propanediol needed to boost the preservative’s efficacy at one-half their recommended use level
Zemea Propanediol Improves Sensorial Attributes

% Subjects Strongly Agree or Agree

Attributes

Spreads Easily
No Greasy Feeling
No Tackiness
No Filming
Soft Feeling
Absorbs Easily
Feels Comfortable
Smooth Feeling
Pleasant Experience
Skin Feels Moisturized

Zemea Propanediol
Propylene Glycol
Butylene Glycol
Glycerin
Introduction
Introduction

Three new deodorant formulations were developed using high concentration levels of Zemea® propanediol and a unique solubilizer to solve key challenges when formulating

• Clear, Natural Deodorant Stick
• Conventional Roll-On Antiperspirant
• Clear Roll-On Antiperspirant
Formulating Clear, Natural Deodorant Sticks
Formulating Clear, Natural Deodorant Sticks

<table>
<thead>
<tr>
<th>Why a Natural Deodorant Sticks?</th>
<th>Classic Deodorant Sticks</th>
<th>Challenges with Deodorant Sticks</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Propylene glycol sensitivity</td>
<td>• Clear to translucent</td>
<td>• Clarity</td>
</tr>
<tr>
<td>• Triclosan aversion</td>
<td>• Based on propylene glycol, water, and sodium sterate</td>
<td>• Durability</td>
</tr>
<tr>
<td>• PEG-free trend</td>
<td>• Triclosan for deodorancy</td>
<td>• Aesthetics</td>
</tr>
<tr>
<td>• Natural bias</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# Formulation of Deodorant Stick

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ingredients (wt, %)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Distilled Water</td>
<td>54.5%</td>
<td>44.5%</td>
<td>34.5%</td>
<td>22.5%</td>
<td>45.25%</td>
<td>43.25%</td>
<td>35.5%</td>
<td>33.5%</td>
<td>31.5%</td>
<td>31%</td>
<td>16%</td>
</tr>
<tr>
<td></td>
<td>Zemea® propanediol</td>
<td>30%</td>
<td>40%</td>
<td>50%</td>
<td>60%</td>
<td>45%</td>
<td>45%</td>
<td>45%</td>
<td>45%</td>
<td>45%</td>
<td>45%</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td>Sodium Hydroxide (10% Sol)</td>
<td>9.5%</td>
<td>9.5%</td>
<td>9.5%</td>
<td>9.5%</td>
<td>3.75%</td>
<td>4.75%</td>
<td>9.5%</td>
<td>9.5%</td>
<td>9.5%</td>
<td>9.5%</td>
<td>9.5%</td>
</tr>
<tr>
<td>B</td>
<td>Stearic Acid</td>
<td>6%</td>
<td>6%</td>
<td>6%</td>
<td>6%</td>
<td>2%</td>
<td>3%</td>
<td>6%</td>
<td>6%</td>
<td>6%</td>
<td>6%</td>
<td>6%</td>
</tr>
<tr>
<td>C</td>
<td>POLYALDO® 10-1-CCKFG</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2%</td>
<td>4%</td>
<td>4%</td>
<td>4%</td>
<td>6%</td>
<td>8%</td>
<td>8%</td>
<td>8%</td>
</tr>
<tr>
<td>D</td>
<td>Fragrance</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

**Opaque** | **Clarity**

Low | High

**Procedure:**
- Add phase A in a clean beaker and heat to 85-95°C.
- Add phase B into phase A and continuously mix the mixture at high temperature (85-95°C). A clear solution will be observed.
- Add the water that was evaporated from heating and add phase C into the clear mixture.
- Reduce the heat to 80°C and add phase D with stirring.
- Transfer to packaging at 80°C.

**Discussion:**
- Zemea® propanediol used at 60% provided shorter duration for mixture to solidify and a firmer deodorant stick.
- Combining Zemea® propanediol and a unique solubilizer provides greater stick clarity at room temperature and the use of higher fragrance loads without the use of triclosan.
Formulating Conventional and Clear Antiperspirant Roll-Ons
# Formulating Conventional and Clear Antiperspirant Roll-Ons

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Convenient, effective</td>
<td>• Opaque thin emulsion</td>
<td>• Stability</td>
</tr>
<tr>
<td>• No flaking or whitening</td>
<td>• Non-volatile solvent/emollient phase</td>
<td>• Roller ball issues</td>
</tr>
<tr>
<td>• Ease of production</td>
<td>• High level of aluminum salt</td>
<td>• Aesthetics</td>
</tr>
<tr>
<td>• Fragrance delivery</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


**Conventional Opaque Antiperspirant Roll-On Emulsion**

<table>
<thead>
<tr>
<th>Phase</th>
<th>INCI</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Wt, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cyclopentasiloxane</td>
<td>SF 1202</td>
<td>Momentive</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>Steareth-2</td>
<td>Brij® S2</td>
<td>Croda</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>Steareth-21</td>
<td>Brij® S721</td>
<td>Croda</td>
<td>2%</td>
</tr>
<tr>
<td>B</td>
<td>Propanediol</td>
<td>Zemea®</td>
<td>DuPont Tate &amp; Lyle</td>
<td>7%</td>
</tr>
<tr>
<td></td>
<td>Silica</td>
<td>Cab-O-Sil® M5</td>
<td>Cabot</td>
<td>0.2%</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>-</td>
<td>-</td>
<td>68.8%</td>
</tr>
<tr>
<td>C</td>
<td>Aluminum Chlorohydrate</td>
<td>ACH-321</td>
<td>Summit-Reheis</td>
<td>15%</td>
</tr>
</tbody>
</table>

**Procedure:**
- Add phase A into a clean beaker and heat until the wax is completely melted.
- Prepare phase B in another beaker and heat to 70°C.
- Add phase A into phase B with stirring.
- Remove the mixture from hot plate and continue to stir.
- Once the emulsion is formed, add phase C slowly into the emulsion and mix until the ACH is completely dissolved.
- Transfer the emulsion to a roll-on container when it cools to room temperature.

**Discussion:**
Smooth-feeling, non-sticky, quick-drying opaque and clear roll-on antiperspirant formulations obtained through use of Zemea® propanediol.

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**Clear Antiperspirant Roll-On Solution**

<table>
<thead>
<tr>
<th>Phase</th>
<th>INCI</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Wt, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Polyglyceryl-10 Caprylate/caprate</td>
<td>POLYALDO® 10-1-CC KFG</td>
<td>Lonza</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>Propanediol</td>
<td>Zemea®</td>
<td>DuPont Tate &amp; Lyle</td>
<td>10%</td>
</tr>
<tr>
<td>B</td>
<td>Fragrance</td>
<td>-</td>
<td>-</td>
<td>0.5%</td>
</tr>
<tr>
<td>C</td>
<td>Water</td>
<td>-</td>
<td>-</td>
<td>69.5%</td>
</tr>
<tr>
<td>D</td>
<td>Aluminum Chlorohydrate</td>
<td>ACH-321</td>
<td>Summit-Reheis</td>
<td>15%</td>
</tr>
</tbody>
</table>

**Procedure:**
- Add phase A together in a beaker and mix well.
- Add phase B into phase A with stirring.
- Add phase C into phase (AB) and mix homogeneously. The mixture is clear at room temperature.
- Finally, add phase D slowly into phase (ABC) with mixing until all the ACH is completely dissolved.
Conclusion
Conclusion

• Zemea® propanediol works well as a replacement for other glycols in deodorant and antiperspirant applications

• Zemea® propanediol helps formulators solve key challenges of clarity, stability, aesthetics, and durability

• Zemea® propanediol works well with solubilizers, and is an effective solvent for aluminum salts

• Zemea® propanediol improves skin moisturization and sensory aesthetics without causing skin irritation

• Zemea® propanediol can reduce water activity and boost preservative efficacy
Zemea® in over 2000 Products Globally

Skin Care:
• **Cleansers**
  • Facial Cleansers
  • Body Wash
  • Shower Gels
  • Anti-Acne
  • Hand Sanitizers
• **Moisturizers**
  • Moisturizing Lotions
  • Anti-aging Serum
  • Skin Care Masks
  • Eye Creams
  • Scar Massage Gel
• **Sun Care**
  • Sunscreen Lotions
  • Sunscreen Wipes
• **Baby Care Products**
• **Men’s Skin Care Products**

Hair Care:
• Shampoo
• Conditioner
• Various Styling Products

Toiletries:
• **Deodorants**
• Oral Care Products
• Personal Lubricants

Cosmetics:
• Foundation
• Concealer
• Mascara
• Makeup Remover

Other Ingredients:
• Natural Esters
• Fragrances
• Natural Preservatives
• Botanical Extracts
Zemea® Propanediol Registrations

Approvals/Certifications:
• ECOCERT
• Natural Products Association (NPA)
• Health Canada
• EPA’s Design for the Environment (DfE)
• 100% Bio-based – USDA BioPreferred® Program
• Halal
• Kosher
• sGRAS

Registrations:
• INCI Name: Propanediol
• EINECS Number: 207-997-3
• CAS Number: 504-63-2
• REACH Registration Number: 01-2119489383-28-0000
Denis Burlaud

EMEA Sales Executive

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www.duponttateandlyle.com
FATTY-ACID CAPPED OLIGOMERIC PROPYLENE SUCCINATES
Purpose:

• We have completed a project on the proof of concept of producing propylene succinates of varying molecular weights that were end-capped with various fatty acids.

• These oligomers are 100% bio-based and show promise in cosmetic application upon initial screening and property measurements.

• We believe this type of approach demonstrates a “tunable” architecture with many possibilities.

• In the spirit of an open innovation approach to the market we are publishing this data early to encourage formulation development on these unique materials and welcome further development of these materials.
Synthesized 24 Fatty-acid End Capped Oligomeric Propylene Succinates

**Oligomer synthesis**
- Three classes of oligomeric propylene succinates have been synthesized:

  - **High**: $M_w \approx 2700$ Da
  - **Medium**: $M_w \approx 1800$ Da
  - **Low**: $M_w \approx 900$ Da

**Fatty-acid endcapping – “Extreme” Examples**

$$2 \text{RCOOH} + \text{HO-}\begin{array}{c} \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \end{array}\text{HO} \rightarrow \text{HO-}\begin{array}{c} \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \end{array}\text{RCO}_{2}\text{OH}$$

**Reaction Conditions**
- EDCI, DMAP
- DCM, rt
## Properties: from fully amorphous to semi-crystalline polymers, from viscous oils to waxy solids

<table>
<thead>
<tr>
<th></th>
<th>Fatty-acid end-capping</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C8-Caprylic</strong></td>
<td><strong>C10 - Capric</strong></td>
</tr>
<tr>
<td>Low Mw</td>
<td>Medium Mw</td>
</tr>
<tr>
<td>High Mw</td>
<td>Low Mw</td>
</tr>
<tr>
<td>Medium Mw</td>
<td>High Mw</td>
</tr>
<tr>
<td><strong>C12-Lauric</strong></td>
<td></td>
</tr>
<tr>
<td>Low Mw</td>
<td>Medium Mw</td>
</tr>
<tr>
<td>High Mw</td>
<td></td>
</tr>
<tr>
<td><strong>C18</strong></td>
<td></td>
</tr>
<tr>
<td>Stearic (unbranched)</td>
<td>Oleic (unsaturated)</td>
</tr>
<tr>
<td>Isostearic (branched)</td>
<td></td>
</tr>
</tbody>
</table>

### Odor
- **C8-Caprylic**: odorless or faint odor (faint ethyl acetate-like)
- **C10-Capric**: garlic
- **C12-Lauric**: odorless or faint odor
- **C18**: low odor (faint ethyl acetate odor)

### Color
- **C8-Caprylic**: colorless to pale yellow/amber
- **C10-Capric**: colorless/pale yellow
- **C12-Lauric**: white
- **C18**: colorless viscous liquid to waxy off-white/pale yellow solids

### Texture
- **C8-Caprylic**: oil
- **C10-Capric**: oil
- **C12-Lauric**: solid wax
- **C18**: waxy/paste-like

### Structure
- **C8-Caprylic**: amorphous (no melting temperature observed) with very low Tg (< -45 °C) or no observable Tg
- **C10-Capric**: Semi crystalline with low melting temperatures (<25 °C) and low Tg (-35 to -50 °C)
- **C12-Lauric**: Semi crystalline with melting temperatures around 40 °C (at the high MW end) and low Tg (-40 to -60 °C); low Mw oligomers do not exhibit observable Tm or Tg
- **C18**: amorphous (no Tm observed) with very low Tg (< -50 °C) or no observable Tg (at lowest Mw)

### Td
- thermally stable to at least 200 °C

### General Trends

**Low Mw**
- Viscous oil
- Colorless/White

**High Mw**
- Wax/Solid
- Off-White/Yellow
Solubility: Opportunity or Challenge?

- Solubility assessed at **10 % w/v, 1 % w/v, and 0.1 % w/v**
- No differences observed for different Mw

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Fatty-acid end-capping</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C2-Acetate</td>
</tr>
<tr>
<td><strong>Cosmetic</strong></td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>glycerol</td>
<td>Insoluble</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Dimethicone</td>
<td>soluble</td>
</tr>
<tr>
<td>Capric/Caprylic</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>N/A</td>
</tr>
<tr>
<td>Isopropyl palmitate</td>
<td>Insoluble</td>
</tr>
<tr>
<td>mineral oil</td>
<td>soluble</td>
</tr>
<tr>
<td>Tween 20</td>
<td>soluble</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>Insoluble</td>
</tr>
<tr>
<td><strong>Organic</strong></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>soluble</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>soluble</td>
</tr>
<tr>
<td>acetone</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>dimethyl sulfoxide</td>
<td>soluble</td>
</tr>
<tr>
<td>n-hexane</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Surface tension: Good surfactants, especially those based on long-chain fatty acids

<table>
<thead>
<tr>
<th></th>
<th>High $M_w$</th>
<th>Medium $M_w$</th>
<th>Low $M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic (C2)</td>
<td>37.8</td>
<td>41.6</td>
<td>41.9</td>
</tr>
<tr>
<td>Caprylic (C8)</td>
<td>37.0</td>
<td>38.9</td>
<td>40.6</td>
</tr>
<tr>
<td>Capric (C10)</td>
<td>37.7</td>
<td>39.7</td>
<td>39.9</td>
</tr>
<tr>
<td>Lauric (C12)</td>
<td>31.7</td>
<td>36.5</td>
<td>38.3</td>
</tr>
<tr>
<td>Stearic (C18)</td>
<td>30.6</td>
<td>29.1</td>
<td>31.0</td>
</tr>
<tr>
<td>Isostearic (C18)</td>
<td>30.4</td>
<td>28.4</td>
<td>29.4</td>
</tr>
<tr>
<td>Oleic (C18)</td>
<td>30.5</td>
<td>33.6</td>
<td>33.7</td>
</tr>
<tr>
<td>Behenic (C22)</td>
<td>27.6</td>
<td>31.4</td>
<td>34.6</td>
</tr>
</tbody>
</table>

Measurements taken after drop equilibration for ca. 5 min at RT

- Surface tension of 1 % w/w solutions of FA-capped oligomers measured by pendant drop shape analysis
- All oligomers reduce surface tension of DMSO
- Longer chain fatty-acids result in larger reduction of surface tension.
Viscosity: Tunable property

Viscosities of dilute polymer solutions in dichloromethane were measured at different concentrations using an electromagnetic viscometer.

- 1 % w/v solutions of FA-capped OPS exhibited no change in the viscosity of the solution relative to pure solvent:
  - Possibly good for cosmetic formulation purposes
  - Oligomers at 1 wt % may not significantly alter the viscosity of the formula

- 2.5 % w/v solutions of FA-capped OPS exhibited only a modest increase in solution viscosity:
  - Relative viscosities were generally between 1.1 - 1.25.
  - Higher MW oligomers tended to yield higher solution viscosities
  - Little differences between different fatty acid-capped oligomers within same Mw range
Summary: Formulate to Innovate

Alcohol-terminated oligomeric propylene succinates of varying molecular weight were synthesized and end-capped with various fatty acids (a total of 24 unique oligomers were prepared):

- FA-capped OPSs were characterized by NMR and FT-IR spectroscopies.
- Thermal properties (Tg, Tm, Td) were analyzed by DSC and TGA
- Solution behavior of these oligomers was studied
- Surface tension and viscosity of dilute polymer solutions were measured confirming that longer fatty acid chains had greater surfactant properties
- Viscosity of dilute solutions unchanged at low oligomer concentrations: at higher concentrations, viscosity changed more as a function of molecular weight than fatty acid chain length

Next step is formulation work on these unique materials, we are providing this data to accelerate innovation at our customers
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