Colonial Chemical

Formulating Dioxane Free

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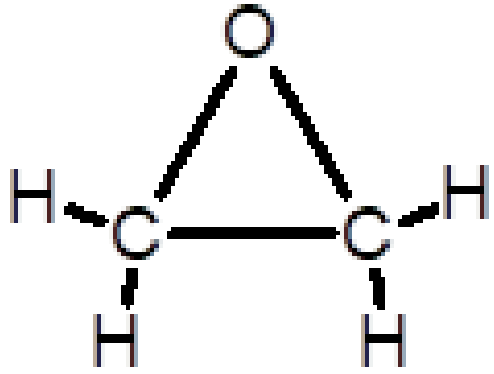
WASH YOUR HANDS

Outline

- What is ethoxylation?
- Common ethoxylates and their uses
- Dioxane issues and regulations
- Application-specific replacements
  - Workhorse emulsification
  - Fragrance solubilization
  - Low irritation cleansers
  - Surfactant thickening
  - Emolliency/Refatting (rinse-off)
- Conclusions.

What is ethoxylation?

- Addition of ethylene oxide (EO) to base molecule
- Most commonly performed on alcohols
  - Natural or synthetic
  - Fatty or short chain
- Production of glycols (ethylene glycol, polyethylene glycol)
- Production of ethanolamines
  - MEA, TEA, DEA
- Production of isethionic acid
- Typically produces new alcohol which can be further reacted
  - More EO
  - Sulfation
  - Carboxylation
  - Esterification.



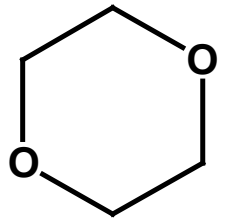
Ethylene Oxide

Common Ethoxylates and Their Uses

Ingredient	Function
Steareth-2, Steareth-20	Workhorse o/w Emulsifier Combo
Polysorbates	Workhorse o/w Emulsifiers
PEG-40 Hydrogenated Castor Oil	Fragrance Solubilization (End Use)
Alkylphenol Ethoxylates	Fragrance Solubilization (In Fragrance)
Sodium Laureth Sulfate	Lower Irritation Sulfate
Poloxamer	Zero Irritation Surfactant (Oral Care)
PEG-150 Distearate	Surfactant Thickening
PEG-120 Methyl Glucose Dioleate	Surfactant Thickening
PEG-7 Glyceryl Cocoate	Emollient/refatting (Rinse-Off)
PEG-75 Lanolin	Emollient/refatting (Rinse-Off)
Dimethicone PEG-7 Isostearate	Emollient/refatting (Leave-on)
PEG-5 Castor Oil	Emollient/refatting (Leave-on)

Dioxane Issues

For many ethoxylates,
a by-product is 1,4-Dioxane:

2   

Ethylene Oxide : C_2H_4O

1,4-Dioxane : $C_4H_8O_2$

Dioxane Issues

- 1,4-Dioxane is a CMR (Carcinogenic, mutagenic and reprotoxic) substance
  - NTP “reasonably anticipated to be a human carcinogen”
  - IARC 2A “possibly carcinogenic to humans”
  - Known to be a carcinogen in animals
- Multiple organ toxicant (liver, kidneys, central nervous system)
- Toxic to aquatic plants and invertebrates
- Moderately persistent in the environment
- Regulated exposure limits in household and cosmetic products vary worldwide
- Many states have reporting requirements for children’s products (MN, ME, OR, VT, WA).

Dioxane Found in Cosmetics

Levels Reported	Number of Products	Percent of Total
0.0 – 1.0 ppm	111	65%
1.1 – 5.0 ppm	32	19%
5.1 – 10.0 ppm	14	8%
10.1 – 25.0 ppm	11	6%
>25.1 ppm	2 (35.2, 35.0 ppm)	1%

SCCS (Scientific Committee on Consumer Safety), Opinion on the Report of the ICCR Working Group: Considerations on Acceptable Trace Level of 1,4-Dioxane in Cosmetic Products, 15 December 2015, SCCS/1570/15

Worldwide Cosmetic and Household Exposure Limits

Agency	Daily Exposure Level	Comments
Canada – CMP assessment	85 µg/day	Aggregate exposure, 100% inhalation, 3.4% dermal absorption. Based on LOAEL/NOAEL
Europe	217 µg/day	Aggregate exposure, 3 scenarios, 100% inhalation, 50% dermal absorption. Based on NOAEL
Japan	4.3 µg/day	General population exposure estimation using Monte Carlo simulation. Based on MOE from NOAEL
Australia	420 µg/day	Aggregate exposure from up to 10 products. Based on NOAEL
California (Proposition 65)	30 µg/day	Based on LCR of 10^{-5}
SCCS	55 µg/day	Based on LCR of 10^{-5}

SCCS (Scientific Committee on Consumer Safety), Opinion on the Report of the ICCR Working Group: Considerations on Acceptable Trace Level of 1,4-Dioxane in Cosmetic Products, 15 December 2015, SCCS/1570/15

Dioxane Limits in Cosmetics

- Based on this information, the following limits have been proposed or enacted for cosmetics

- EU: SCCS opinion from 2015 sets safe limit at 10ppm
- ASEAN: 25ppm limit by June 19, 2020, 10ppm limit by June 19, 2023
- FDA: No guidance but use ICCR info
- California: Safe Cosmetics Act requires notification of products with Prop 65 contaminant
  Recent efforts point toward 10ppm limit
- NY State: Cosmetics: 10ppm limit by Dec 31, 2022
  Personal Care: 2ppm limit by Dec 31, 2022, 1ppm limit by Dec 31, 2023.

- Others??

Dioxane-Free Replacements

Considerations for Replacement Selection

- Bio-renewable content
- Toxicity
  - Human
  - Environmental
- Brand positioning
- Ease of use
- Efficiency
- Cost.

Workhorse Emulsification – Small Molecules

- **Glyceryl Stearate with Stearic Acid**
  - Key benefit: 100% naturally derived
  - Key drawback: pH sensitive Stearic Acid
- **Polyglyceryl Esters**
  - Key benefit: Wide variety
  - Key drawback: Generally darker in color
- **Amino Acid Esters**
  - Key benefit: Can be all naturally derived
  - Key drawback: Pricey
- **Phosphate Esters**
  - Key benefit: High purity
  - Key drawback: Phosphate name.

Workhorse Emulsification – Hydrophobically Modified Polymers

- **Synthetic (acrylates)**
  - Key benefit: low cost
  - Key drawback: poor sustainability (currently)

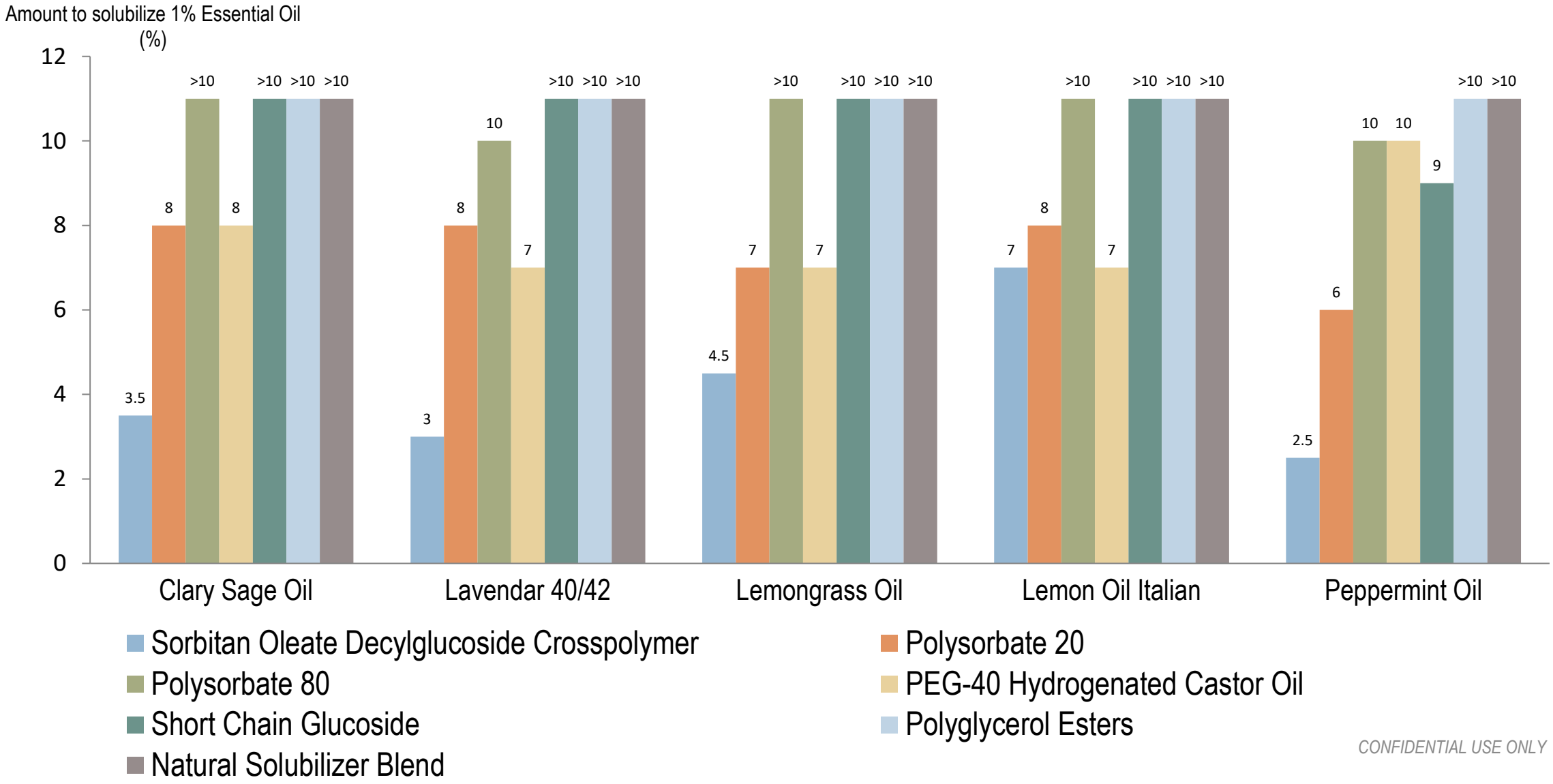
- **Natural (cellulosics, crosspolymers)**
  - Key benefit: biobased content
  - Key drawback: cost

- **Inorganic (silicones)**
  - Key benefit: luxurious feel
  - Key drawback: negative perception.

Fragrance Solubilization

- Some emulsifiers can function as fragrance “solubilizers”
- Fragrance solubilization is really micro-emulsification
- Typically looking for high HLB emulsifiers
- **Polyglyceryl esters**
  - Key benefit: High biobased content
  - Key drawback: No “workhorse” product yet
- **Small molecules**
  - Key benefit: Ease of handling
  - Key drawback: Few choices
- **Surfactant combinations**
  - Key benefit: Optimized performance
  - Key drawback: Adds several ingredients.

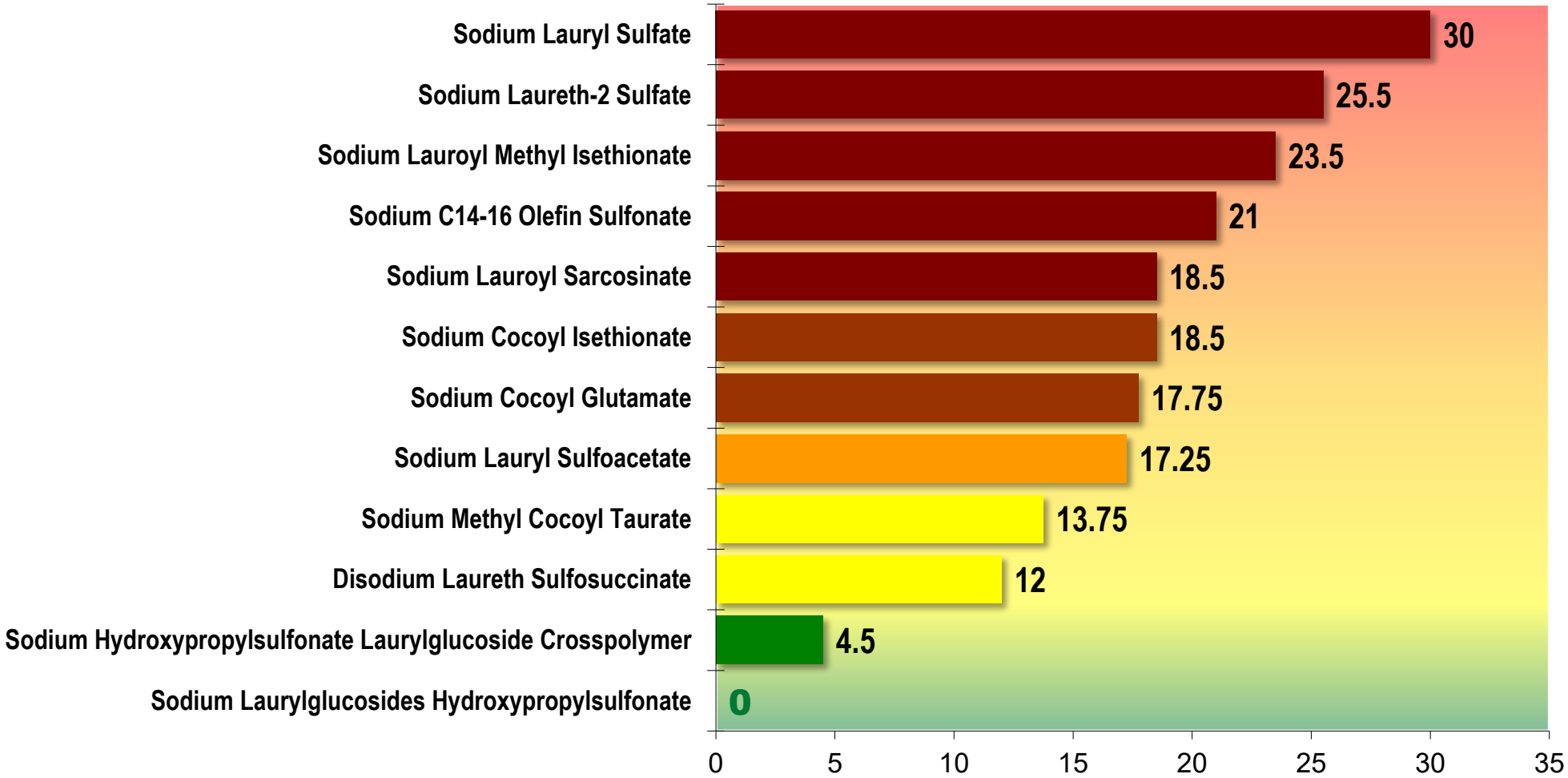
Comparative Efficacy of Solubilizers - premixed oil with solubilizer



Low Irritation Cleansers

- **Alkyl Glucosides**
  - Key benefit: 100% biobased
  - Key drawback: Difficult to formulate with
- **Alkyl Glucoside Derivatives**
  - Key benefit: Expanded application range
  - Key drawback: Few suppliers
- **Sulfosuccinates**
  - Key benefit: Good foam possible
  - Key drawback: Poor stability
- **Amino Acid Surfactants**
  - Key benefit: Excellent stability
  - Key drawback: Costly.

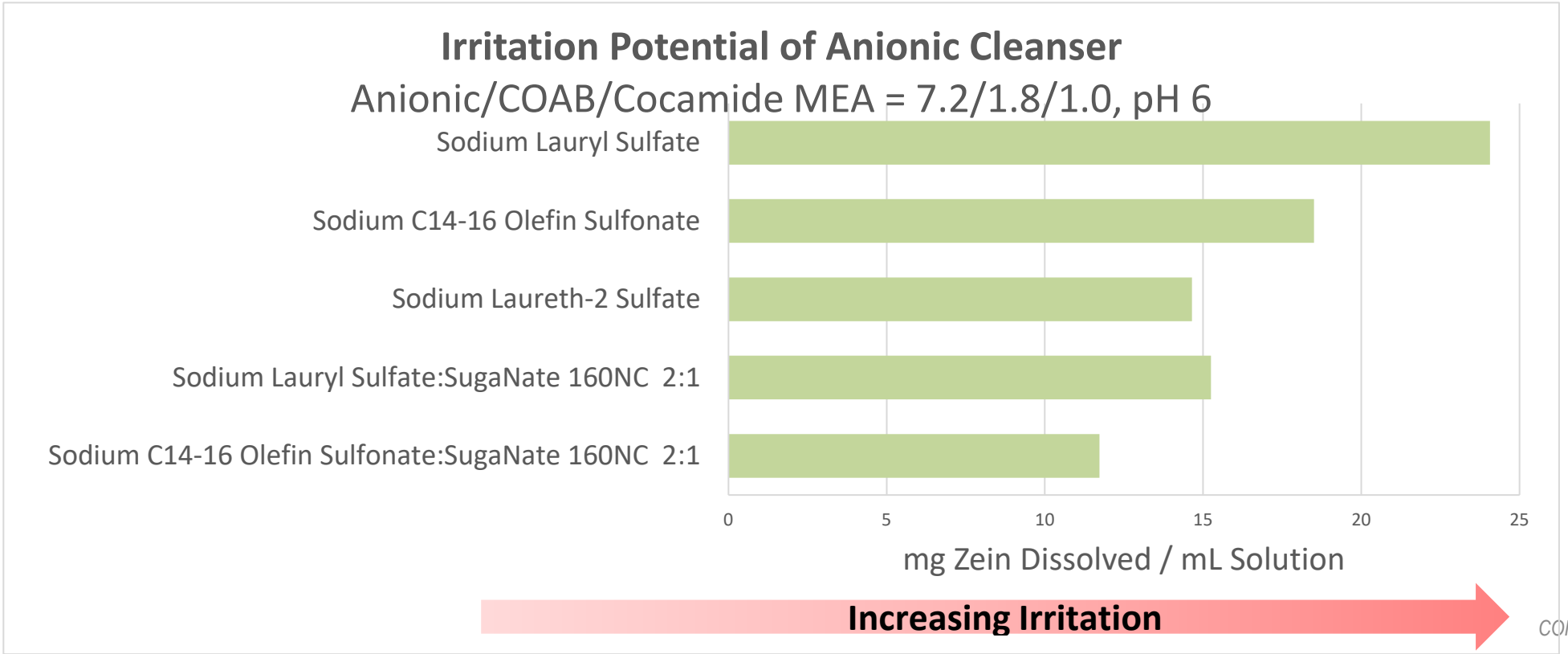
Comparative Irritation of Several Sulfates and Replacements – HET-CAM



10% solids, pH 5.5 - 6.5

Using A Zero-Irritation Surfactant to Replace SLES

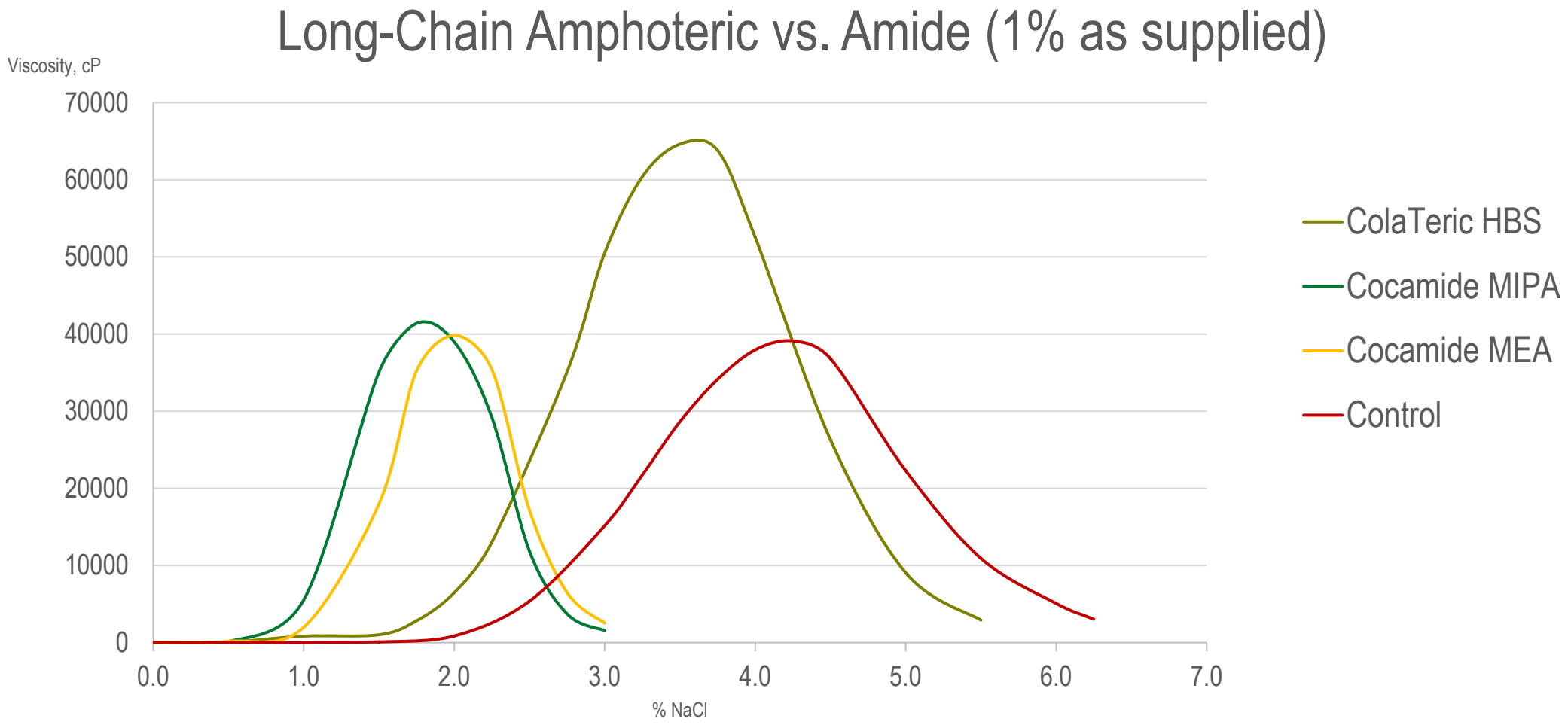
- Adding a zero-irritation surfactant (Sodium Laurylglucosides Hydroxypropylsulfonate) to SLS and AOS demonstrates the potential for a strong mollifying effect on irritation
- The in-vitro zein protein data suggest that Sodium Laurylglucosides Hydroxypropylsulfonate can be a very useful tool for reducing irritation in economical cleansing systems



Surfactant Thickening

- **Synthetic Polymers (HASE/HEUR)**
  - Key benefit: Highly customized performance
  - Key drawback: Mostly or purely petrochemical feedstocks
- **Alkanolamides**
  - Key benefit: Economical
  - Key drawback: Potential secondary amine issues
- **Amine Oxides**
  - Key benefit: Excellent performance
  - Key drawback: Not well characterized for personal care
- **Long-Chain Amphoterics**
  - Key benefit: Very effective viscosity boosters
  - Key drawback: Low active products or contain solvents.

Comparative Efficacy of Nonionics vs Long-Chain Amphoteric



Emolliency/Refatting

- **Glyceryl Oleate/Polyglyceryl Oleate**
  - Key benefit: 100% biobased
  - Key drawback: Easy to overwhelm system
- **Phosphate amphoterics**
  - Key benefit: Very high substantivity
  - Key drawback: Negative association with phosphate
- **Lecithin/Phospholipids**
  - Key benefit: All natural
  - Key drawback: Can be pricey
- **Long-Chain Amphoterics**
  - Key benefit: Economical
  - Key drawback: Lack of efficacy data

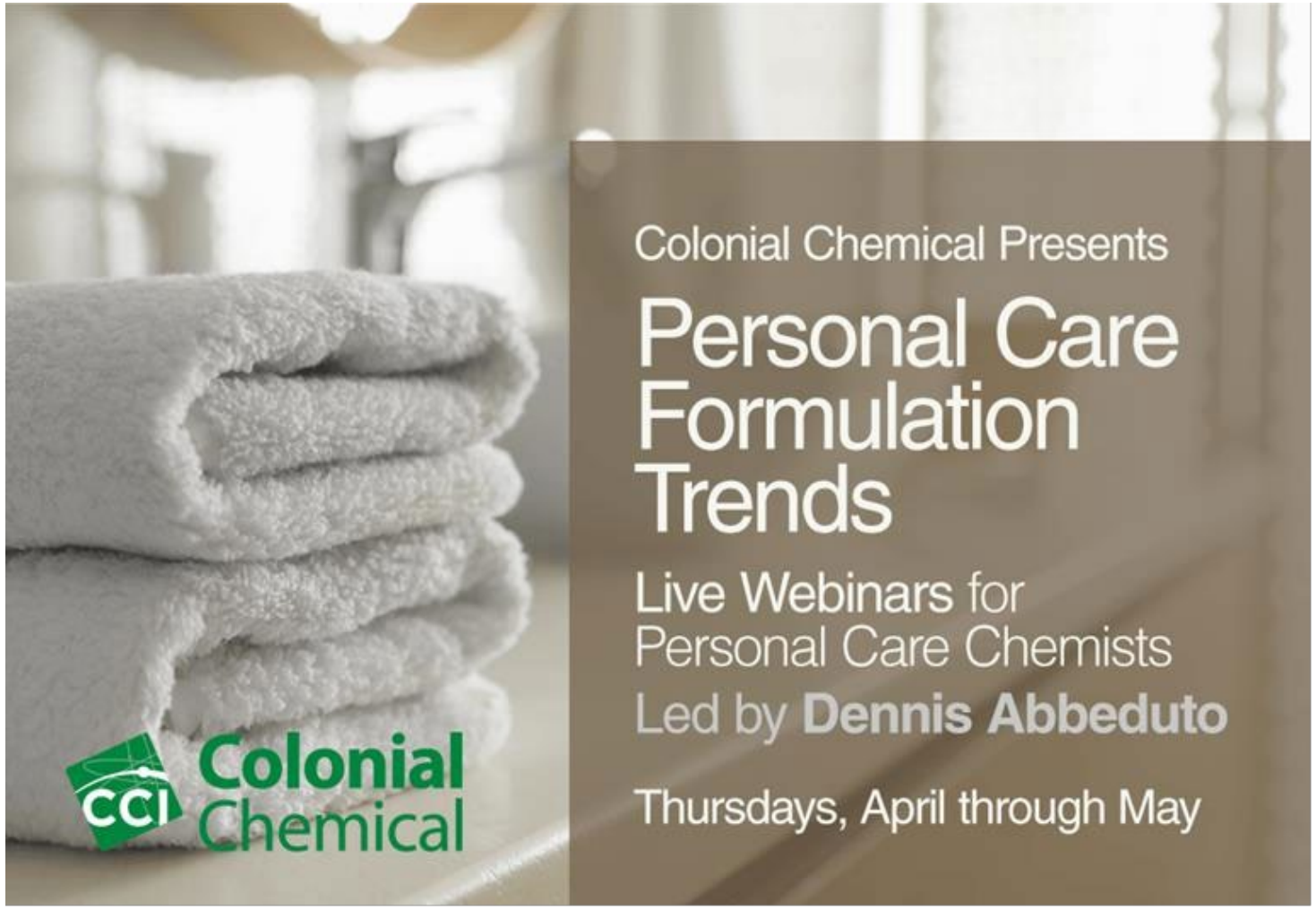
Wrap-up

- Ethoxylation has been a useful tool for achieving high performance products
- Concerns related to 1,4 Dioxane have driven levels found in cosmetics down
- New laws may make it even harder to incorporate ethoxylates into formulations
- Many tools already exist to assist formulators as they move away from ethoxylates
- Formulators need to weigh pros and cons of each solution to determine what's best for them.

Webinar Series – Coming Events

- May 21 – Dioxane-Free Formulas
- May 28 – Sulfate-Free Formulas
- June 11 – The Other Side of Fear
- June 25 – Reduced Irritation in Rinse off Cleansers

- **https://bit.ly/2XXTbEO**



Thank you!

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