Managing 1,4-Dioxane

How BASF's FLEX Solutions can Impact your Business

Dr. Michael Capracotta
Camille Miller
Jack Bordonaro

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Today's presenters

Dr. Mike Capracotta

Mike is the Technical Manager for BASF's North American Home Care and I&I technical service group and earned his Bachelor's in Chemistry from Clemson University and his PhD in Solid State Chemistry from North Carolina State University. Mike is a core member of BASF's task force that is developing solutions for managing 1,4-dioxane and is based in Wyandotte, Michigan.

Camille Miller

Camille is the Marketing and New Business Development Manager of Industrial and Institutional Cleaning at BASF Corporation in Florham Park, NJ. She is responsible for managing new product introductions, developing digital marketing tools, conducting market analysis and steering channel execution within the I&I market. Camille has held various positions in Supply Chain and Marketing with BASF over the past nine years

Jack Bordonaro

Jack is responsible for product line launches, aligning media outlets, releasing market reports, and overseeing the HCII Website. Jack has worked previously in BASF's Pharma segment and joined the HCII team in May 2021. He received his Bachelor's in Business with a focus on Marketing Analytics from the University of North Carolina Charlotte. Jack's added support has helped the team further digitalization in this changing market.

Agenda

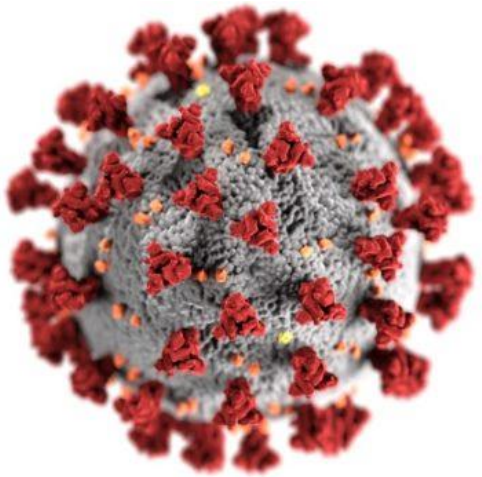
- **The background behind 1,4-Dioxane and how it is created**
- **Noteworthy Regulatory News concerning 1,4-Dioxane**
- **BASF's Newly Expanded FLEX Solutions of Free and Low 1,4-Dioxane Products**

Population Trends Driving Sustainable Needs

Population Size / Urbanization

Growth of the Middle Class

Pandemic: Covid-19



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BASF We create chemistry

Flex Formulation flexibility for low 1,4 - Dioxane requirements

Does Your Formula Include Any of These Ingredients?

Ingredients Made From Ethylene Oxide (EO)

- Alkyl Ether Sulfates (SLES)
- Ethoxylated alcohols
- PEGs
- Castor oil ethoxylates
- Fatty alcohol mixed with ethoxylates
- Glycol distearates
- Glycol distearate blends

If you answered “Yes”, then you probably have 1,4-Dioxane in your products and are subject to regulatory requirements!

What exactly is 1,4-Dioxane?

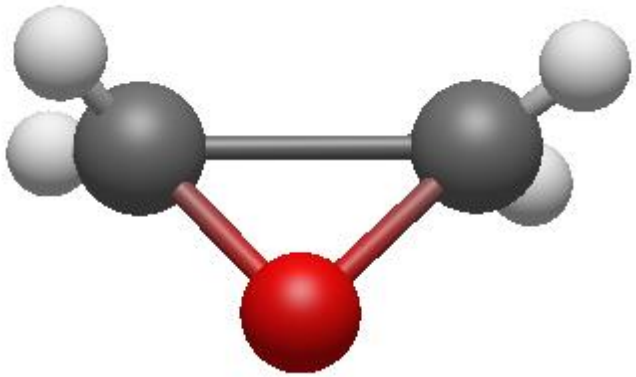
- 1,4-Dioxane is a **synthetic molecule** used as **stabilizer and solvent** in commercial and industrial applications.
- 1,4-Dioxane is a ***by-product*** of the manufacturing process of certain surfactants produced with **ethylene oxide**
  - ***By-product****: A chemical formed in the manufacturing process of a desired product. By-products* ***inevitably occur*** *in most chemical reactions, they can be minimized, but are usually impossible to prevent completely.*
- Found as an **impurity** in deodorants, shampoos, toothpastes, cleaning products, paints, etc.
- 1,4-Dioxane is **volatile and fully water soluble**

https://www.epa.gov/sites/production/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf
https://www.fda.gov/cosmetics/potential-contaminants-cosmetics/14-dioxane-cosmetics-manufacturing-byproduct

Where Does 1,4-Dioxane Come From?

(5x) Ethylene oxide

C_2H_4O



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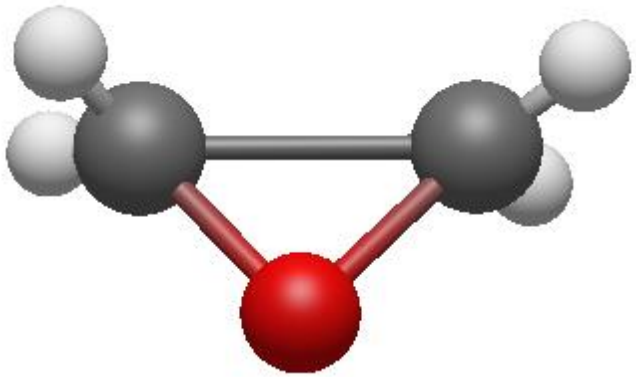
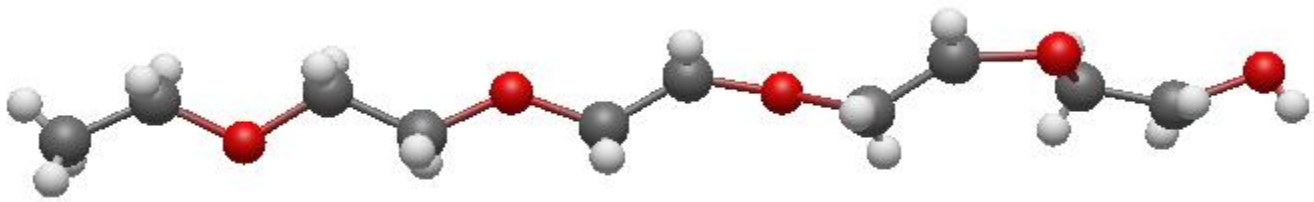




Polymerized Ethylene oxide

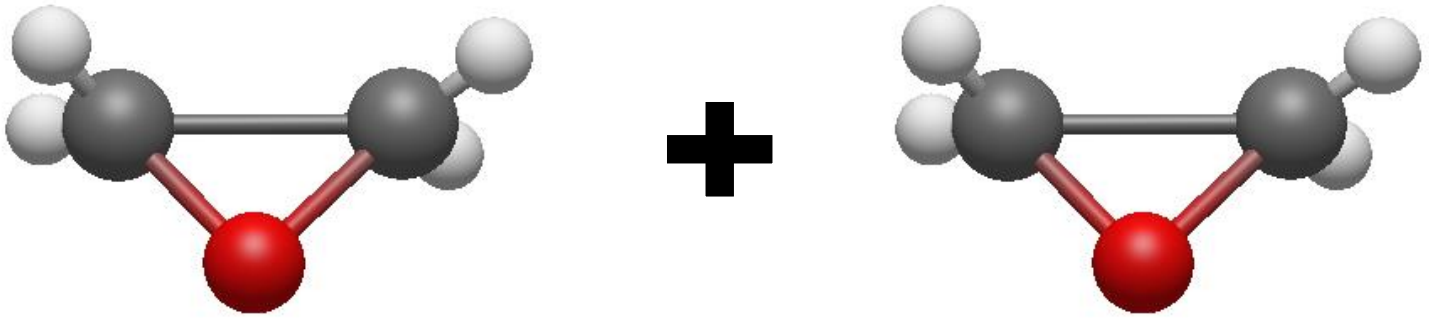
(Polyethylene Glycol, PEG)

$(C_2H_4O)_x$

Where Does 1,4-Dioxane Come From?

Ethylene oxide

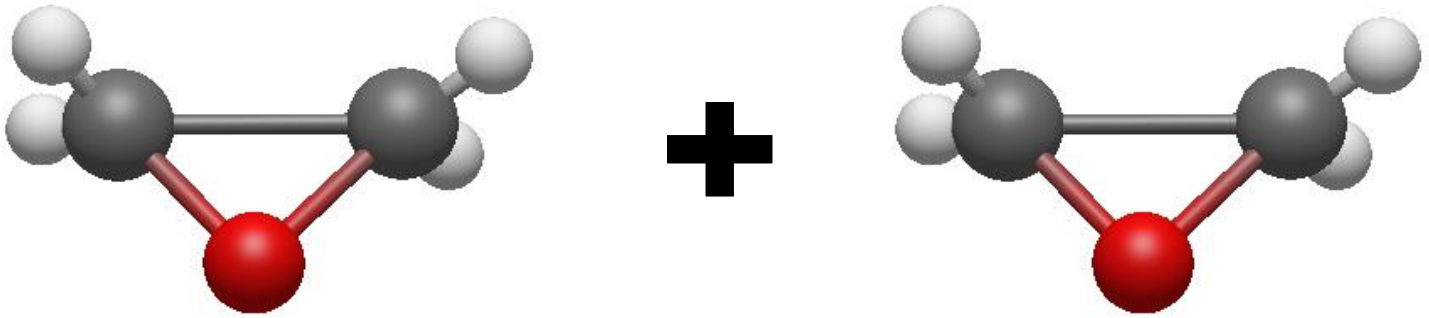
C_2H_4O



Where Does 1,4-Dioxane Come From?

Ethylene oxide

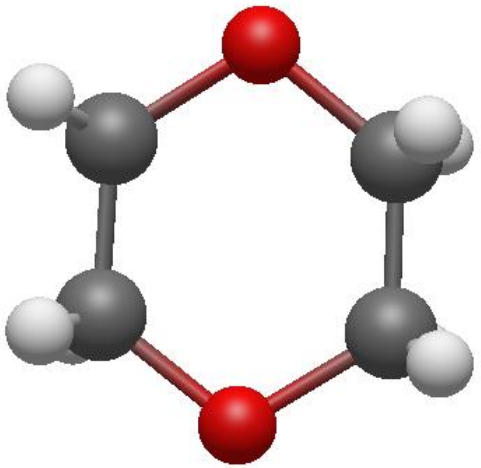
C_2H_4O



Dimerized Ethylene Oxide

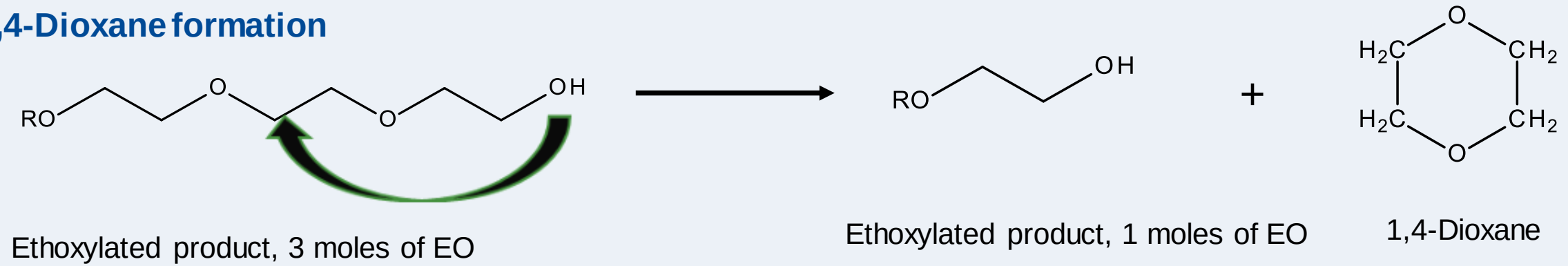
1,4-dioxane

$C_4H_8O_2$



Formation of 1,4-Dioxane from an ethoxylated product

1,4-Dioxane formation



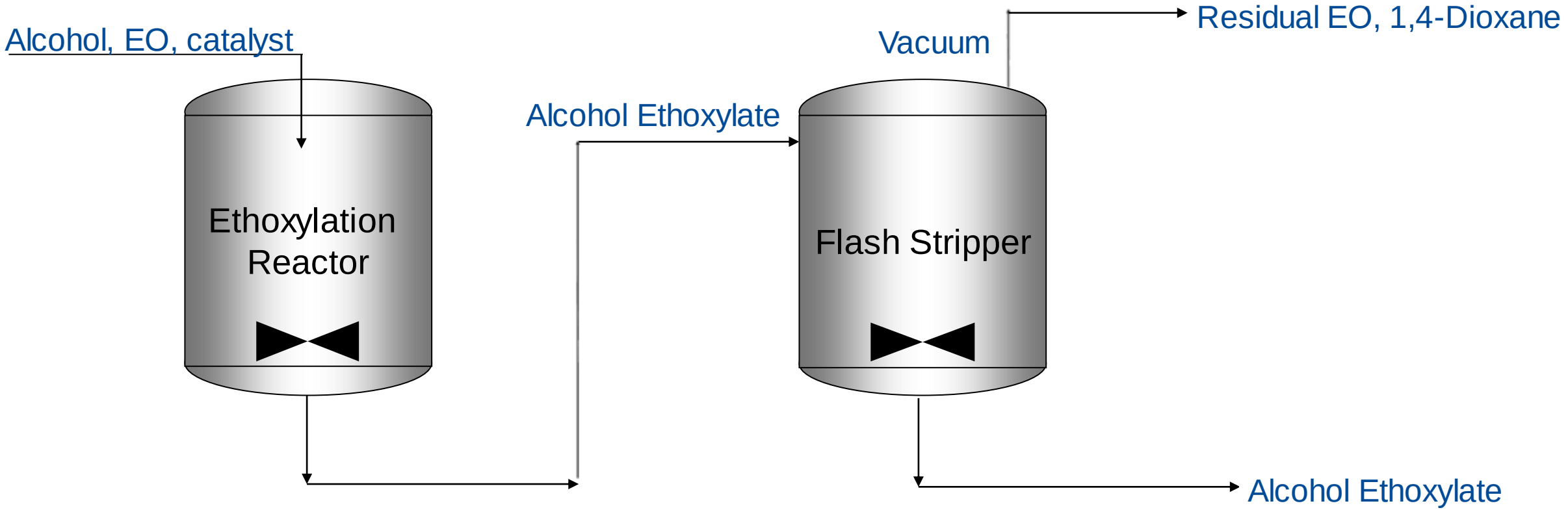
Ethoxylated product, 3 moles of EO

Ethoxylated product, 1 moles of EO

1,4-Dioxane

- **Unintended side reaction**, known as “intramolecular chain transfer” or “backbiting”.
- Two moles of EO are eliminated to form 1,4-Dioxane
- Backbiting can happen once for every 2 moles of EO on the molecule

The Good News: 1,4-Dioxane Content Can Be Reduced!



Ether Sulfates: A Particular Challenge

Ether Sulfates (e.g. SLES) are made in a 2-step process:

Step 1: Ethoxylated Alcohol Sulfation

$$R\text{-}(OCH_2CH_2)_nOH + SO_3 \rightarrow R\text{-}(OCH_2CH_2)_nOSO_3H$$

Alkyl ether
(e.g. lauryl alcohol ethoxylate)

Alkyl ether acid sulfate;
aka “acid ester”

→ Problem 1: Acid Ester is prone to 1,4-Dioxane formation.

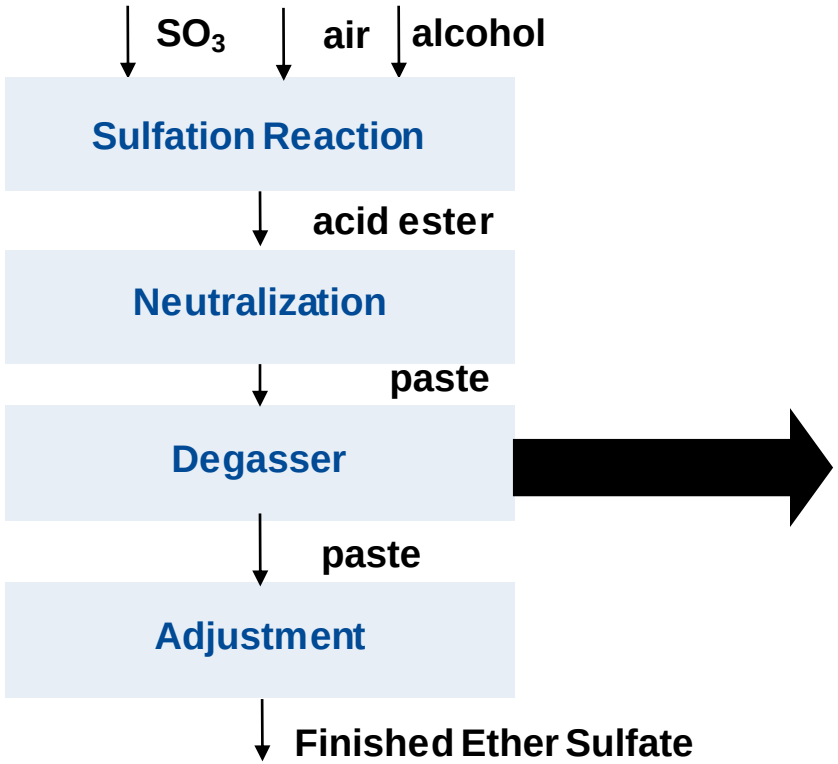
Step 2: Neutralization

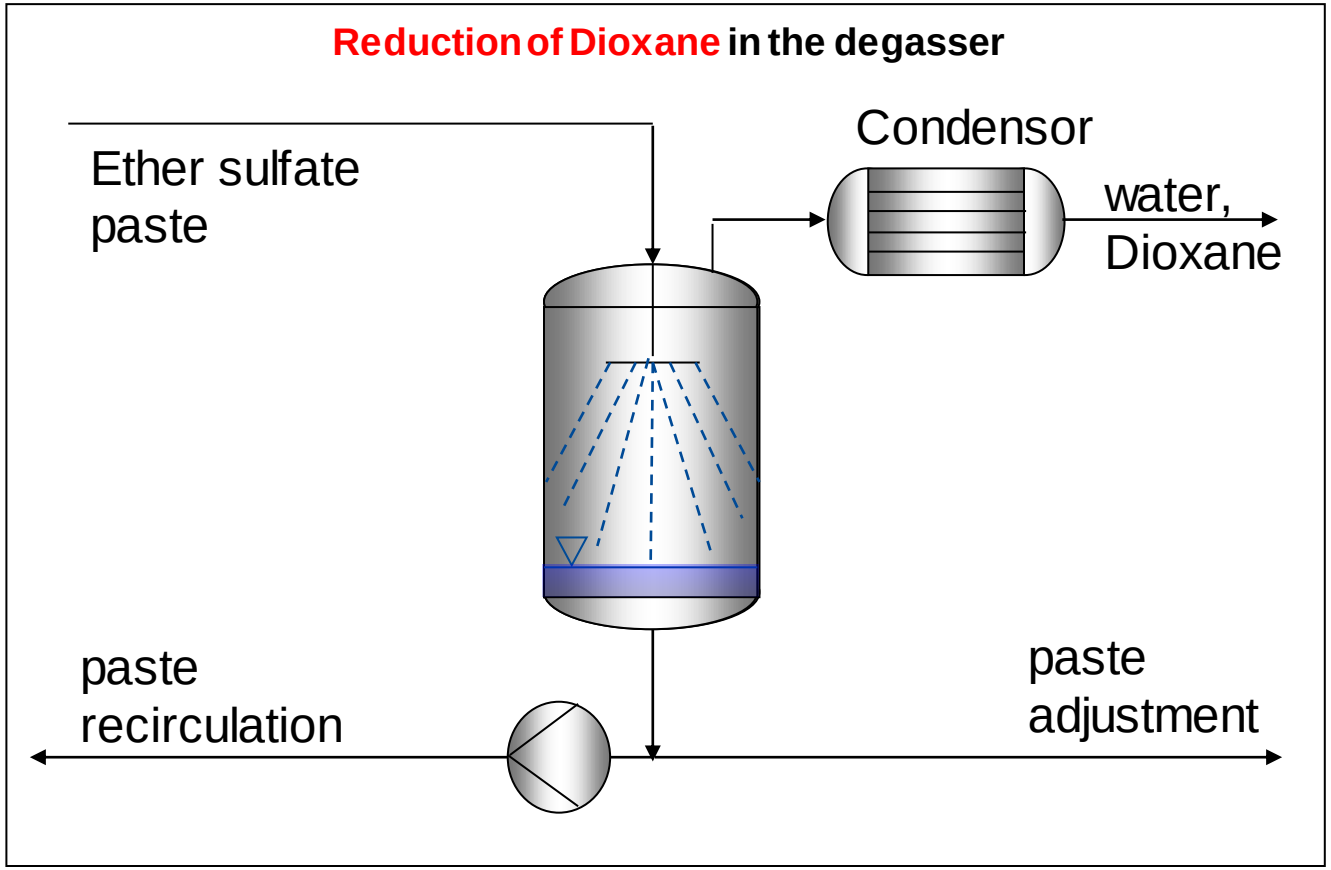
$$R\text{-}(OCH_2CH_2)_nOSO_3H + NaOH \rightarrow R\text{-}(OCH_2CH_2)_nOSO_3Na + H_2O$$

Alkyl ether sulfate
(e.g. Sodium Lauryl ether sulfate, SLES)

→ Problem 2: Presence of water makes 1,4-Dioxane removal much more difficult.

1,4-Dioxane removal from Ether Sulfates by Steam Stripping





Degassing can reduce 1,4-Dioxane by ~50%

Estimated ppm 1,4-Dioxane in I&I Formulations

Typical I&I Manual Detergent			2-36 ppm 1,4-Dioxane
Description	**Typical 1,4-Dioxane level (ppm)**	**Typical Use Levels**	**Contribution of 1,4-Dioxane in the bottle (PPM)**
Alkyl Ether Sulfate (70% active)	20-100	10-20%	2-20
Alcohol Ethoxylate	1-5	0-5%	0-0.25

Typical I&I Liquid Laundry Detergent			2-15 ppm 1,4-Dioxane
Description	**Typical 1,4-Dioxane level (ppm)**	**Typical Use Levels**	**Contribution of 1,4-Dioxane in the bottle (PPM)**
Alcohol Ethoxylates	20-100	10-15%	2-15

So, what is the concern about 1,4-Dioxane?

- The data available from human epidemiological studies is not adequate to evaluate the relationship between human cancer and exposure to 1,4-dioxane.
- The EPA has classified 1,4-Dioxane as **"likely to be carcinogenic to humans"** by all routes of exposure (per EPA IRIS 2013)
- A 2016 report by the Department of Health and Human Services National Toxicology Program (NTP) found that 1,4-dioxane is:
  - "**reasonably anticipated to be a human carcinogen** based on sufficient evidence of carcinogenicity from studies in experimental animals".

https://www.epa.gov/sites/production/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf
https://www.fda.gov/cosmetics/potential-contaminants-cosmetics/14-dioxane-cosmetics-manufacturing-byproduct
https://www.nysenate.gov/legislation/laws/ENV/35-0103

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Elevated 1,4-Dioxane levels found in NY groundwater in 2016

- 2016: the Environmental Protection Agency (EPA) found >/= 1ppb levels of 1,4-Dioxane in groundwater in New York; highest levels are in Long Island.
- EPA risk assessments indicate that the drinking water concentration representing a 1 x 10^{-6} cancer risk level for 1,4-dioxane is 0.35 µg/L (0.35 ppb) (EPA IRIS 2013)
- No federal maximum contaminant level (MCL) for drinking water has been established (EPA 2012). NY State Department of Health working on establishing an MCL for 1,4 dioxane in drinking water.

NY State legislature bill targets Home + Personal Care products

- **June 2019:** New York State Senate and Assembly passed a bill to limit presence of 1,4-Dioxane in **Household Cleaning Products**, Cosmetic products and Personal Care products.
- **Status:** Signed By NY State Governor Cuomo on Dec. 9, 2019.
- **Ongoing Actions:** The annual Waiver Submission period has been open as of October 1st

NY Bill 1,4-Dioxane Limit Restrictions Summarized	
Household Cleaning Products + Personal Care Products	• 2 ppm by Dec. 31, 2022 • 1 ppm by Dec. 31, 2023 • 2025: Department of Environmental Conservation in consultation with the Department of Health can determine, by rule, if the "trace concentration threshold shall be lowered to better protect human health and the environment"
Cosmetic Products	• 10 ppm by Dec. 31, 2022 • 2025: Department of Environmental Conservation in consultation with the Department of Health can determine, by rule, if the "trace concentration threshold shall be lowered to better protect human health and the environment"

Interpretation of NY Law

- A "Household cleaning product" is defined as: Any product, including but not limited to soaps and detergents, containing a surfactant as a wetting or dirt emulsifying agent and used primarily for domestic or commercial cleaning purposes, including but not limited to, the cleansing of fabrics, dishes, food utensils and household and commercial premises.
- NY DEC interprets this to cover:
  - Any product containing a surfactant meant to clean or cleanse
  - Consumer and commercial/institutional, but not industrial
  - Concentrated versions of these products.

https://www.nysenate.gov/legislation/laws/ENV/35-0103

Additional states & legal complexities face Home & Personal Care

California

- California Right to Know Act (2017)
  - CPRKA
  - SB 258
- Manufacturers of cleaning products sold in California must post the following information (and more) on their websites by Jan 2020 and on labels by Jan 2021:
  - "intentionally added" ingredients
  - "nonfunctional constituents" at concentrations at or above 100 ppm
    - 1,4-Dioxane specifically set at >=10ppm
  - CAS
  - functional purpose served of intentionally added ingredient

- Safer Consumer Products Evaluation
  - State Department of Toxic Substances Control (DTSC) is assessing 1,4 Dioxane in HC and PC product(s) through Safer Consumer Products program
  - Estimated to be completed in ~3 years. (2022)

Additional states & legal complexities face Home & Personal Care

New Jersey

- New Jersey Drinking Water Quality Institute voted to recommend establishing a health-based drinking water Maximum Contaminant Level (MCL).
- Developing Drinking Water Standards:
  - No current federal or New Jersey drinking water standards for 1,4-dioxane.
  - Establish a regulatory limit for 1,4-dioxane.
  - Recommend MCL for 1,4 Dioxane of 0.33 ug/L.
  - The NJDEP Commissioner will review the formal recommendation.
    - If accepted, stakeholder and formal rulemaking would be initiated.
  - Once formally regulated, water systems would be required to:
    - monitor for the presence of 1,4-dioxane, and
    - take remediation measures where the levels are exceeded.

 NJDEP - Responding to Emerging Contaminants: 1,4-Dioxane

EPA Works to Revise the TSCA 1,4-D Risk Evaluation

- The final risk evaluation for 1,4-dioxane found that there are unreasonable risks to workers for 13 out of 24 conditions of use (COU)
- EPA did not find an unreasonable risk for the use of 1,4-dioxane as a by-product in consumer cleaning products.
- The EPA under the new administration petitioned to remand the risk evaluation of 1,4-Dioxane.
- The remanded risk evaluation to be completed by the end of 2022.
    - Additional exposure pathways (drinking water and ambient air) and conditions of use.
- Until the revision is completed, the results of the original risk evaluation stand.

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The BASF Response to 1,4-Dioxane

- 6-16-2019: New York State Senate passes bill to limit 1,4-dioxane in Household Cleaning, Cosmetic, and Personal Care Products.
- 11-13-2019: BASF hosts first UL Prospector Educational Webinar on 1,4-dioxane: "Business Leaders Shed Light on 1,4-Dioxane"
- 12-9-2019: Gov. Cuomo signs NY 1,4-dioxane restrictions into law. Also, on this day BASF launches our FLEX program at the HCPA XPAND annual meeting. Initial launch contains 5 low dioxane products. (side comment: the timing was serendipitous not planned)
- 2-3-2020: BASF launches second wave of FLEX products, bringing the total to 10 products.
- Sept 2021: Expansion of FLEX program to include 93 low 1,4-dioxane products. Portfolio now has a Free and Low list.
- 11/3/2021: BASF hosts UL Prospector Webinar on 1,4-Dioxane and our New 2021 portfolio.
- BASF will continue market education on 1,4-dioxane, monitoring regulations, and expanding of FLEX program

BASF's Solution to 1,4-Dioxane: New 2021 FLEX Portfolio

This is an extensive portfolio of ingredients Free of 1,4-Dioxane and ingredients containing Low (<3ppm) levels of 1,4-Dioxane

Free 1,4-Dioxane Certified Ingredients

- 46 Ingredients
- Alternatives to existing products that contain no 1,4-Dioxane
- Chelating Agents, Enzymes, Surfactants & Polymers

Low 1,4-Dioxane Certified Ingredients

- 46 Ingredients
- New alternatives to existing products offer guaranteed low 1,4-Dioxane levels
- certified at batch level on every COA

BASF We create chemistry | Flex Formulation flexibility for low 1,4 - Dioxane requirements

Formulation Expertise

BASF now has over 90 free & low 1,4-Dioxane products in our portfolio. Our experienced formulators can use these products as a toolbox in your final formulations.

What does that mean for you?

We understand:

- The relative risk of formulas
- Ingredients that contribute the most to 1,4-Dioxane levels

BASF Solutions:

- Technical guidance for your reformulation and replacement efforts
- Alternative ingredients that do not contain 1,4-Dioxane
- Formulations Free of or Low in 1,4-Dioxane

BASF We create chemistry | Flex Formulation flexibility for low 1,4 - Dioxane requirements

Start now—Here's how to prioritize:

I&I

Formulations:

- Manual dish
- Liquid Laundry Concentrates
- Rinse Aids
- Degreaser Concentrates

Ingredients:

- Alkyl Ether Sulfate (SLES)
- Ethoxylated alcohols
- Alkoxylated alcohols
- PEGs
- EO/PO Block Copolymers
- Other Polymers containing EO

Home Care

Formulations:

- Manual dish
- Liquid Laundry
- Laundry single-dose
- Fragrance enhancers

Ingredients:

- Alkyl Ether Sulfate (SLES)
- Ethoxylated alcohols
- PEGs
- EO/PO Block Copolymers
- Other Polymers containing EO

Personal Care

Formulations:

- Shampoo
- Hair Pomades/Waxes
- Toothpaste

Ingredients:

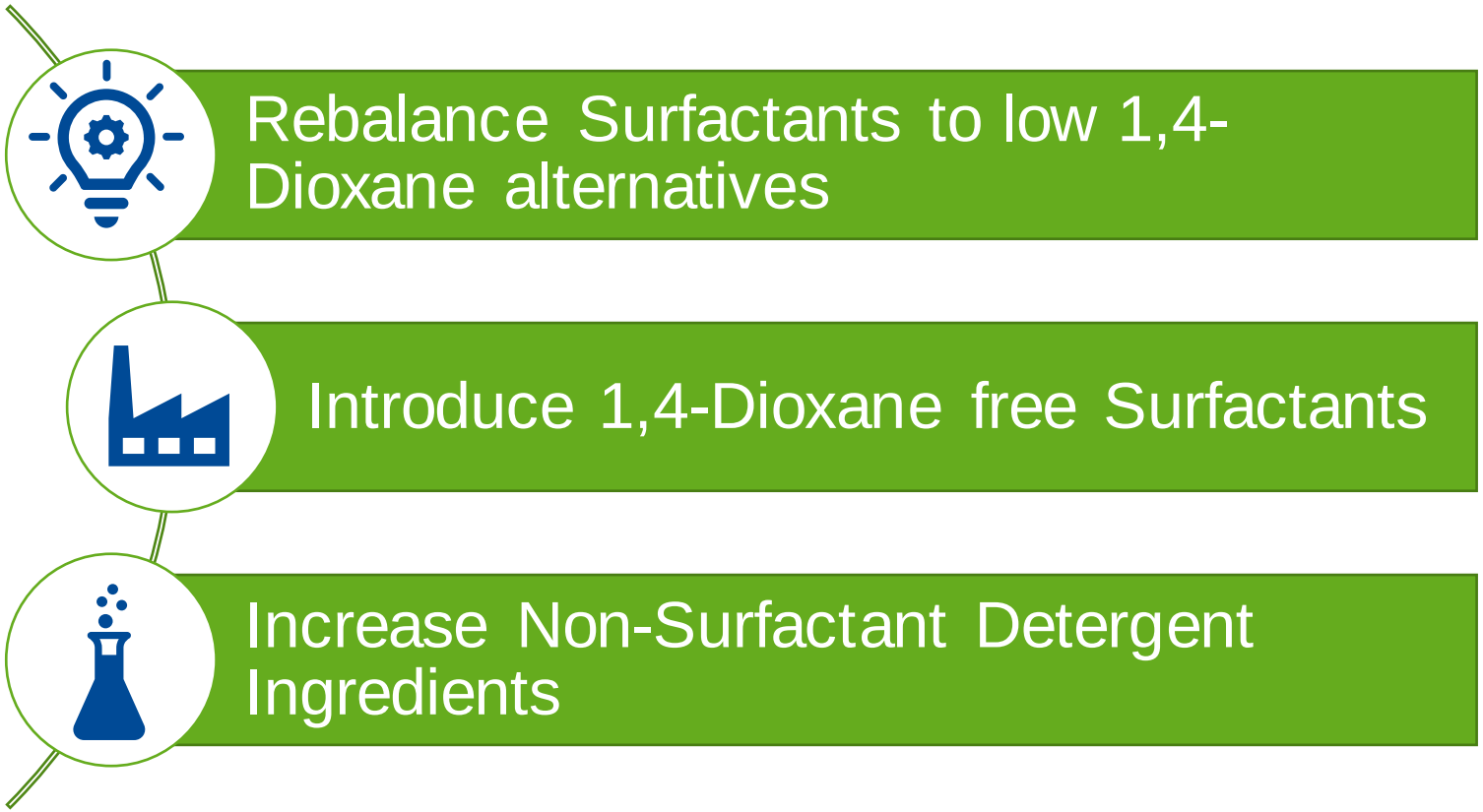
- PEGs and PEG-derivatized castor oils
- Ethoxylated alcohols
- Fatty alcohol mixed with ethoxylates
- Alkyl ether sulfates (SLES)
- Glycol distearates
- Glycol distearate blends
- EO/PO Block Copolymers

Estimated ppm 1,4-Dioxane in I&I Formulations

Typical I&I Manual Detergent			2-36 ppm 1,4-Dioxane
Description	**Typical 1,4-Dioxane level (ppm)**	**Typical Use Levels**	**Contribution of 1,4-Dioxane in the bottle (PPM)**
Alkyl Ether Sulfate (70% active)	20-100	10-20%	2-20
Alcohol Ethoxylate	1-5	0-5%	0-0.25

Typical I&I Liquid Laundry Detergent			1-15 ppm 1,4-Dioxane
Description	**Typical 1,4-Dioxane level (ppm)**	**Typical Use Levels**	**Contribution of 1,4-Dioxane in the bottle (PPM)**
Alcohol Ethoxylates	20-100	10-50%	2-50

3-Fold Strategy for Managing 1,4-Dioxane in your formulations



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Flex Formulation flexibility for low 1,4 - Dioxane requirements

Low 1,4-Dioxane I&I Rinse Aid Formulation

1. Rebalance Surfactants to low 1,4-Dioxane alternatives • Plurafac® SLF 180

Low Temperature Rinse Aid (Formula #35730-25-7)				<1 ppm total
Description	**BASF Products**	**1,4-Dioxane maximum (ppm)**	**Use level (as supplied)**	**1,4 dioxane in the bottle (ppm)**
Water	---	0	q.s.	0
Alcohol Alkoxylate	**Plurafac® SLF 180**	**1**	**25%**	**0.25**
Sodium Xylene Sulfonate (40%)	N/A	0	62.5%	0
Citric Acid (50%)	---	0	q.s.	0

- Full formulation details can be found on BASF's UL Prospector site

BASF We create chemistry | Flex Formulation flexibility for low 1,4 - Dioxane requirements

Low 1,4-Dioxane Concentrated I&I Laundry Formulation

1. Rebalance Surfactants to low 1,4-Dioxane alternatives

- Lutensol® TDA9 FLEX
- Lutensol® XL 80

Commercial Laundry Suds (Formula #35730-81-1)				<1 ppm total
Description	**BASF Products**	**1,4-Dioxane maximum (ppm)**	**Use level (as supplied)**	**1,4 dioxane in the bottle (ppm)**
Water	---	0	44.7%	0
Tridecyl Alcohol Alkoxylate (9 EO)	**Lutensol® TDA 9 FLEX**	**2**	**32%**	**0.64**
Guerbet Alcohol Ethoxylate (8 EO)	**Lutensol® XL 80**	**2**	**8%**	**0.16**
Optical Brightener	Tinopal CBS-X	0	0.3	0
Propylene Glycol	----	0	10	0
Sodium n-octyl sulfate	Texapon 842 UP	0	5	0

- Full formulation details can be found on BASF's UL Prospector site

Low 1,4-Dioxane 6X Liquid Laundry Detergent

1. Rebalance Surfactants with low 1,4-Dioxane alternatives	• Low 1,4-dioxane Sodium Lauryl Ether Sulfate (SLES) • Lutensol® A65N • Dehypon® LS 54
2. Increase 1,4-Dioxane free surfactants	• Glucopon® Surfactants

6X Liquid Laundry Detergent (Formula# C653-169-2C)				<1 ppm
Description	**BASF Products**	**1,4-Dioxane maximum (ppm)**	**Use level (as supplied)**	**1,4 dioxane in the bottle (PPM)**
Water	---	0	38%	0
Propylene Glycol	---	0	3%	0
Fatty Alcohol Alkoxylate	**Dehypon® LS 54 FLEX**	**1**	**24%**	**0.24**
C10-C16 Alkylpolyglucoside	**Glucopon® 420 UP**	**0**	**10.5%**	**0**
C12-C14 Alcohol Ethoxylate	**Lutensol® A65N**	**2**	**10.8%**	**0.22**
Sodium Lauryl Ether Sulfate, 2-mole 70%	---	5	10.5%	0.53
Triethanolamine	---	0	1.5%	0

- Full formulation details can be found on BASF's UL Prospector site

Low 1,4-Dioxane Premium Manual Dishwashing Detergent

1. Rebalance Surfactants with low 1,4-Dioxane alternatives	• Low 1,4-dioxane Sodium Lauryl Ether Sulfate (SLES) • Dioxane Free Sodium Lauryl Sulfate (SLS)
2. Increase 1,4-Dioxane free surfactants	• Glucopon® Surfactants • Dehyton® PK 45 (cocoamidopropyl betaine)
3. Increase non-surfactant detergent ingredients	• Sokalan® HP 20 • Sokalan® HP 30 Booster

Premium Manual Dishwashing Detergent (Formula# 00030-0066-01)				**<0.01 ppm**
Description	**BASF Products**	**1,4-Dioxane maximum (ppm)**	**Use level (as supplied)**	**1,4 dioxane in the bottle (PPM)**
Sodium Lauryl Sulfate (SLS)	---	0	8.64%	0
Nonionic Surfactant (Alkylpolyglucoside)	**Glucopon® 600 UP**	**0**	**7.16%**	**0**
Lauryl Amine Oxide	---	0	4.2%	0
Ethoxylated Polyethyleneimine (PEI)	**Sokalan HP 20**	**2**	**0.33%**	**<0.01**
Sodium Xylene Sulfonate (SXS, 40%)	---	0	10.5%	0
Citric Acid, 50%	---	0	0.8%	0
Water	---	0	q.s. to 100%	0

- Full formulation details can be found on BASF's UL Prospector site

Summary

1,4-Dioxane regulation is here and must be continuously monitored for any changes

Formulators will need to navigate the changing landscape and reassess their ingredient choices

BASF's FLEX program is designed to help meet raw material needs & reformulate for continued success

BASF
We create chemistry

Flex
Formulation flexibility for low 1,4 - Dioxane requirements

Questions?

Technical:
Dr. Mike Capracotta

Marketing / I&I:
Camille Miller

Regulatory:
Marina Filler

Marketing:
Jack Bordonaro

For more info, please visit BASF HCII's UL Prospector site or contact us by email at detergents-cleaners-na@basf.com

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