Industry Misconceptions About Ethoxylated Materials

Ricardo Diez, Ph.D.

"Unofficial Presentation"

Please do not be surprised if I tell you…

MODERN COSMETIC INDUSTRY

1920

Chemical Industry

COSMETICS

REAL COSMETIC INDUSTRY

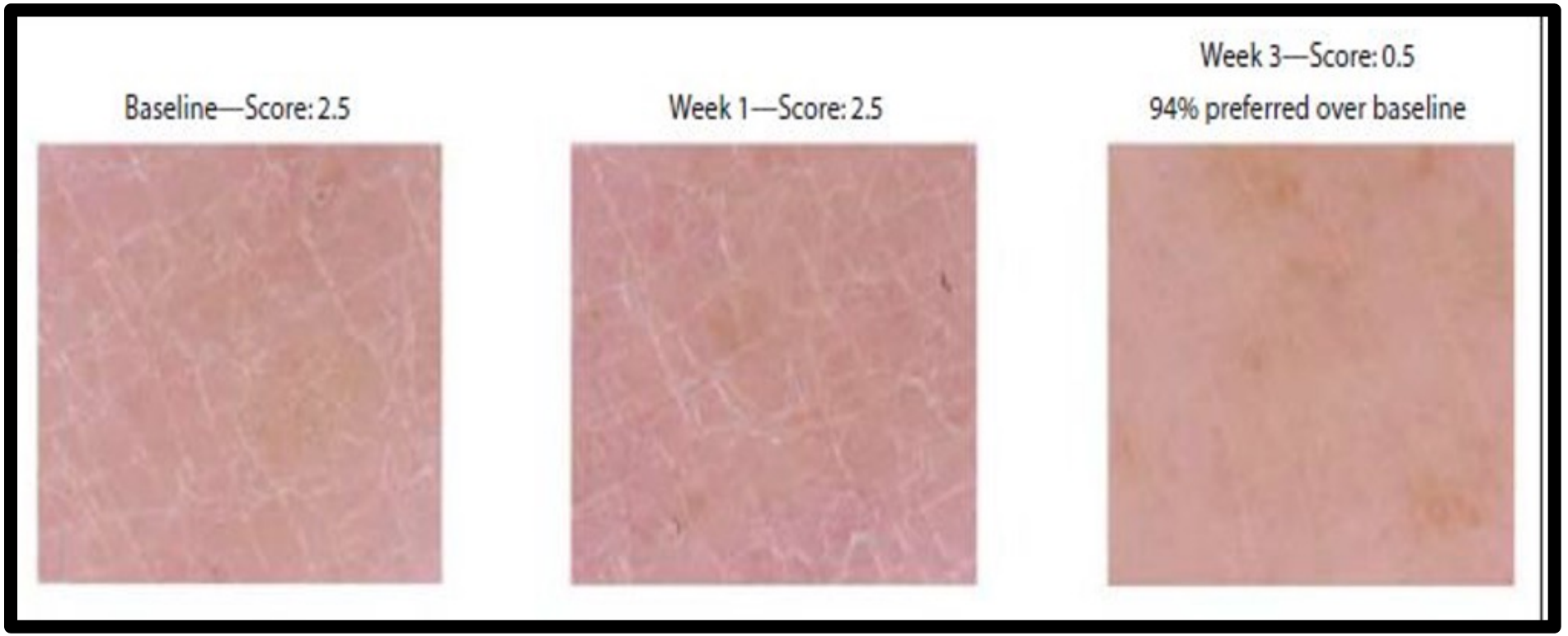
Chemical Industry

COSMETICS

You must prove what you say

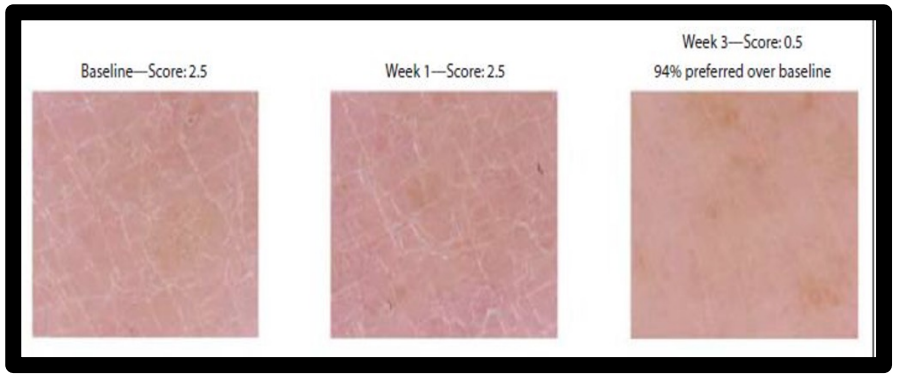
REAL COSMETIC INDUSTRY

REAL COSMETIC INDUSTRY



REAL COSMETIC INDUSTRY

How do you compete with this ?



How do you compete with this ?

ALTERNATIVE Industry → COSMETICS

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1995 “Natural”

2005 ”Sulfate-Free”

2010 “Clean Beauty”

ALTERNATIVE Industry → COSMETICS

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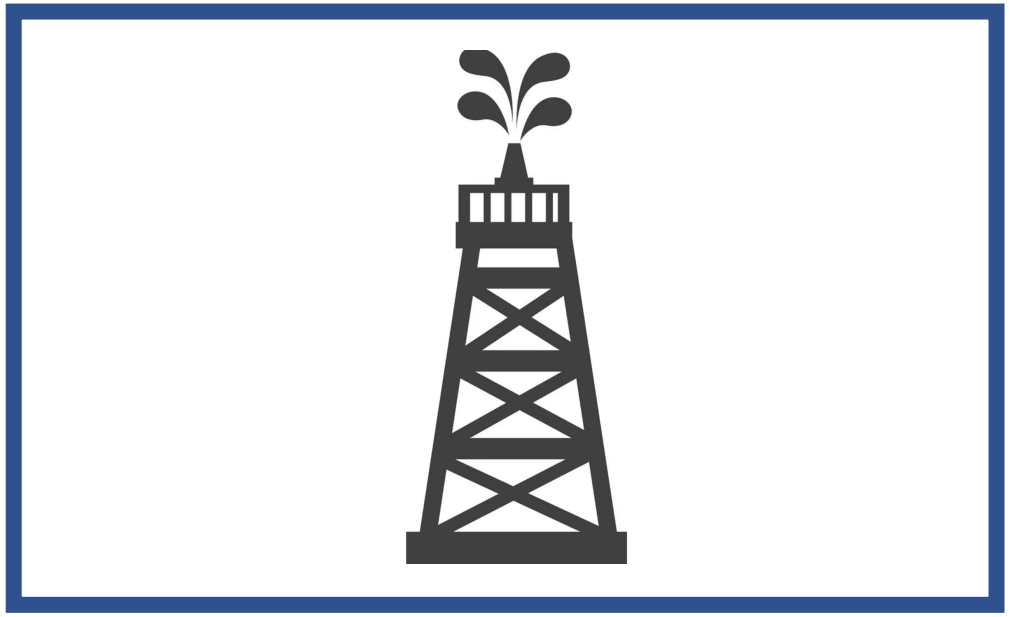
ALTERNATIVE Industry → COSMETICS



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ALTERNATIVE Industry → COSMETICS

NO to "Ether"

1995	"Natural"
2005	"Sulfate-Free"
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The Ordinary Debuts Hair Care Line

Feb 21st, 2022 | By Jacquelyn Mueller, associate editor, Global Cosmetic Industry

"The marketing concept of 'clean' beauty challenges the safety and efficacy of products not deemed 'clean' by **indirectly labeling them as 'dirty'.**

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"The marketing concept of 'clean' beauty challenges the safety and efficacy of products not deemed 'clean' by **indirectly labeling them as 'dirty'.**

It **disregards the important work of scientists** around the world making a monumental effort to evaluate a complete body of evidence to formulate the products that you know and love"

Response of MEDIOCRITY

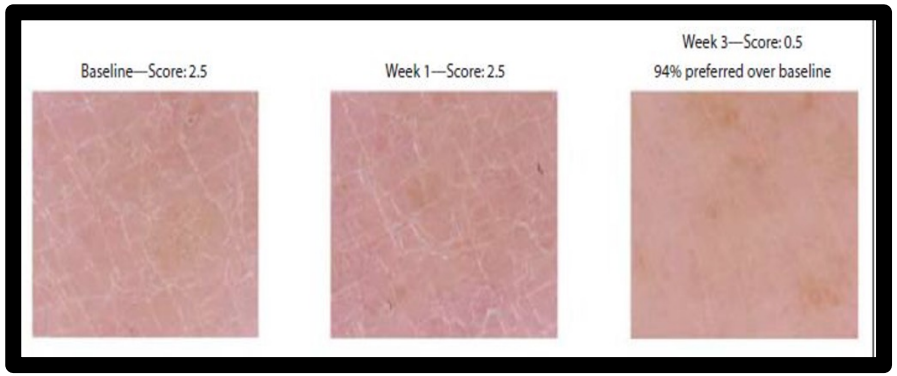
1995 “Natural”

2005 ”Sulfate-Free”

2010 “Clean Beauty”


UN INSTANT
S'IL-VOUS-PLAÎT

Is there something wrong with these products ?



It all depends on their level of 1,4 Dioxane

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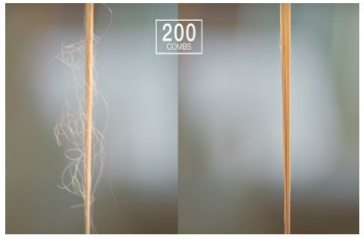
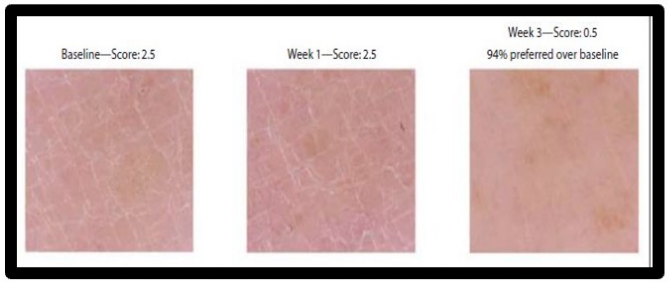




Three “BAD” words

Three "BAD" words

"Ether" → "eth"

Laureth Sulfate

Steareth- 20

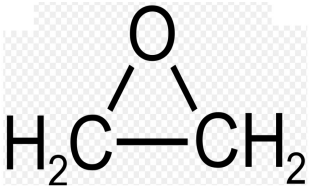
or

PEG

PEG –X 'something'

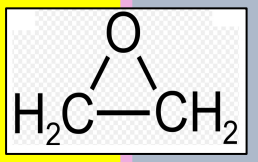
Three “BAD” words

Ethylene Oxide (EO)

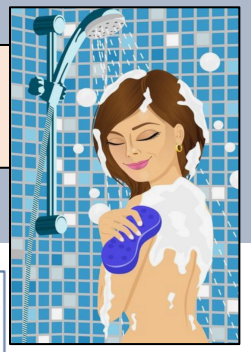


“Ether”

Cosmetic Raw Materials **made with EO** are widely used because of effectiveness



Surfactants



Sulfates

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Ether Sulfates

Sulfonates

Olefin Sulfonates
Isethionates
Taurates

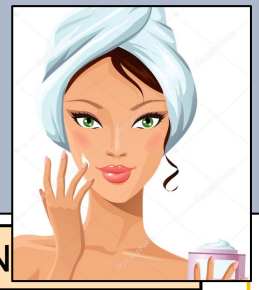
Sulfoacetates
Sulfosuccinates
Sulfolaurates

"Aminoacid" Type

Glycinates
Glutamates
Sarcosinates

Crypto Anionics

Carboxylates
Phosphates



Emulsifiers

AN

Carboxylates (M+)

Sulfates (M+)

CATIONICS

Di stearyl dimonium chloride

CRYPTO-ANIONICS

Alky (Ether) Phosphates (M+)
Alkyl Ether Citrates (M+)

NON-IONICS

Glyceryl Esters →
Sorbitan Esters →
Glucosides Esters →
Sucrose Esters
Polyglyceryl Esters

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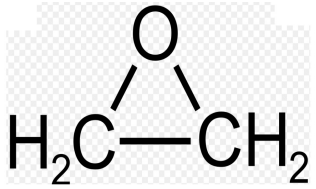
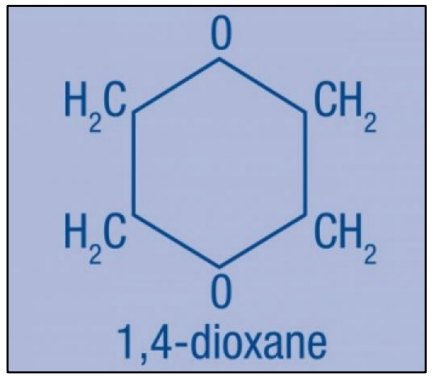


"Ether"

1,4 Dioxane



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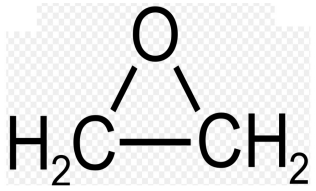

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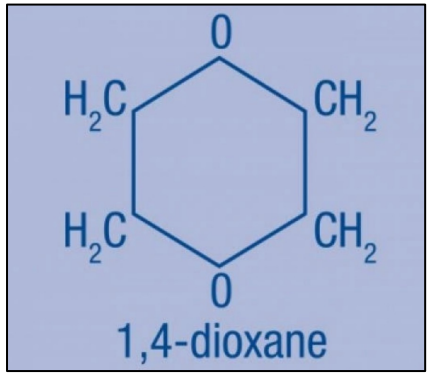
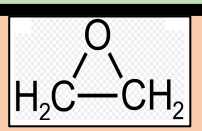
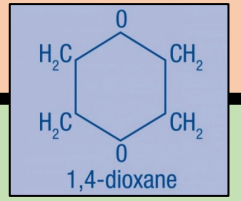


Materilas made with EO



have the **potential to have 1,4 D**



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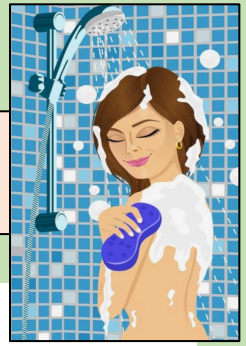

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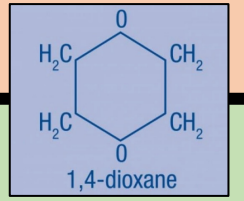
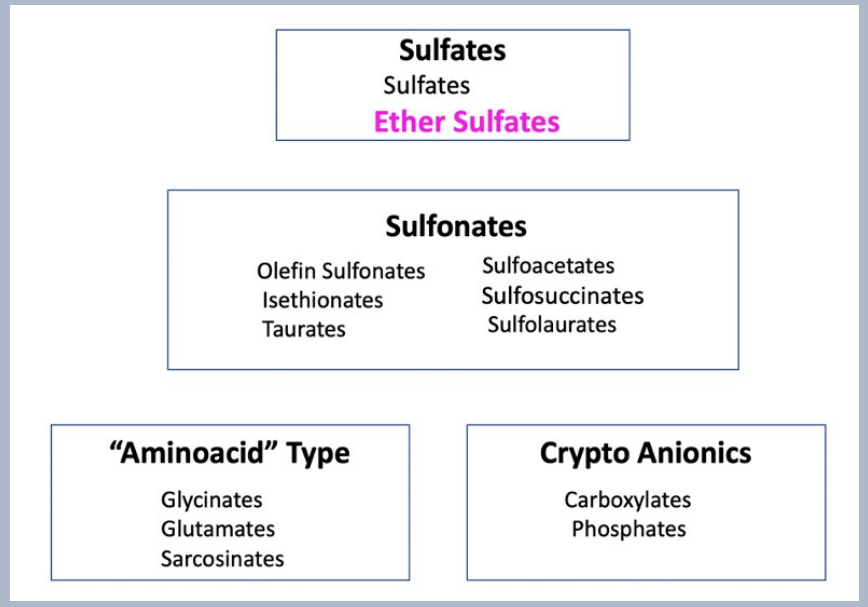
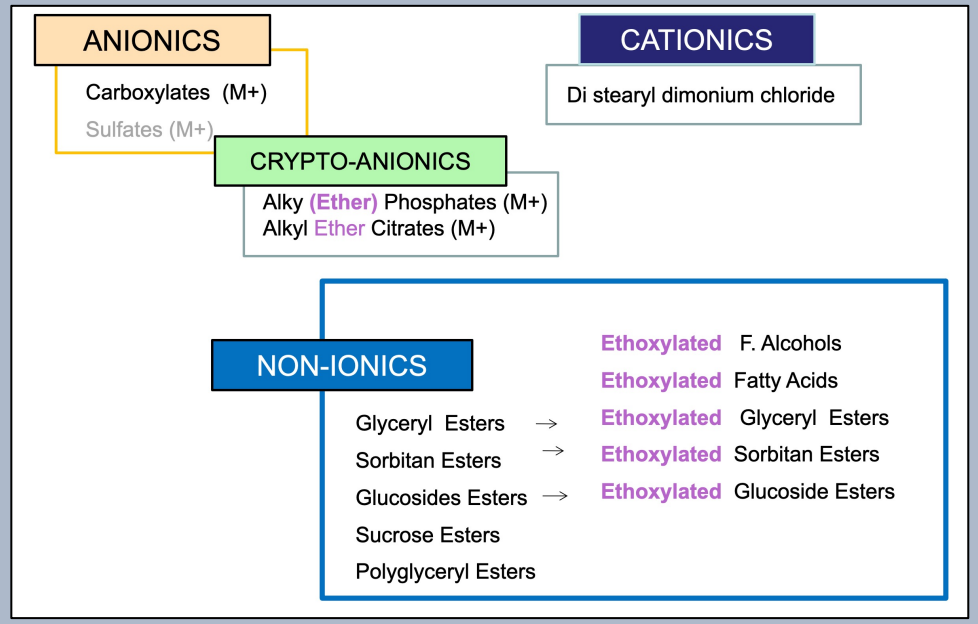


How BAD is this chemical ?

…and what is behind the ….

… NO to “Ether”

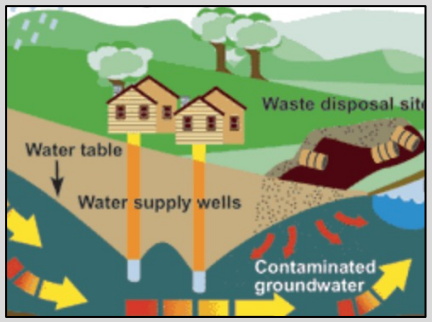




The spill of 1985

WASHTENAW COUNTY Michigan

The spill of 1985



Since 1966, Gelman Sciences (now Pall Corporation) used 1,4-dioxane in their manufacturing process.

In 1985, 1,4-dioxane was found in the drinking water wells

The spill of 1985

"Cosmetic and household products also put 1,4 D in the water supply"

J&J Baby Shampoo

P&G Tide

The spill of 1985

linked together

Cosmetics

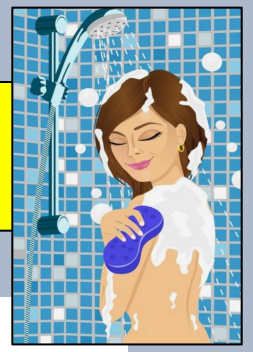
1,4 Dioxane

The spill of 1985

What was the reaction of the cosmetic industry then…?

1- Quantify the problem

High 1,4 D



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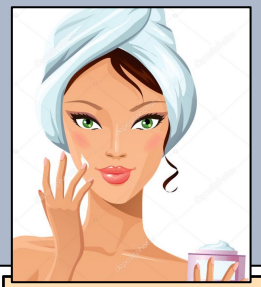

Very low 1,4 D

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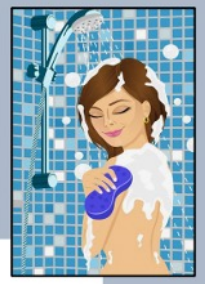
2- Develop technology to reduce 1,4 D

High 1,4 D



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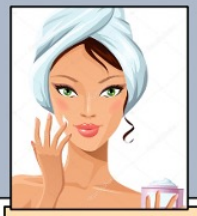

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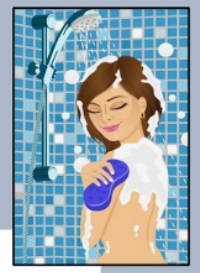

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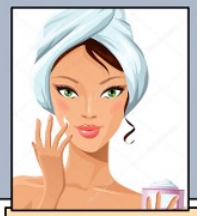

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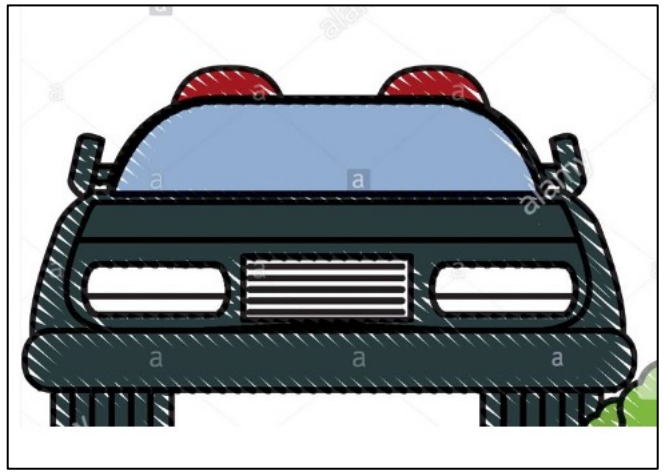
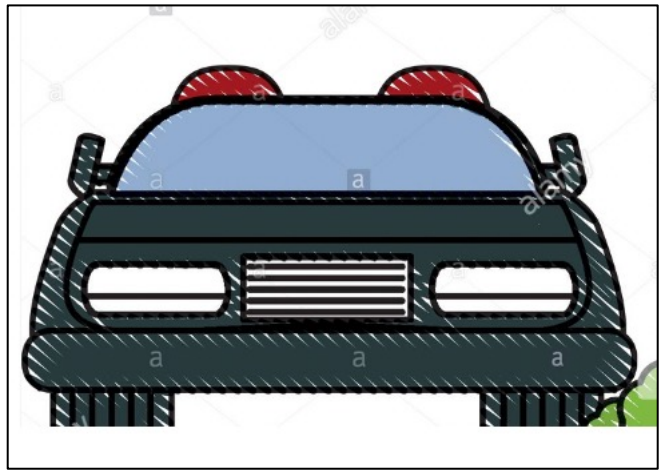



P
PAY
PARKING

“Free”



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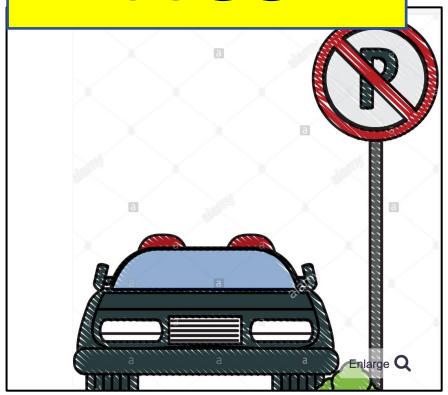

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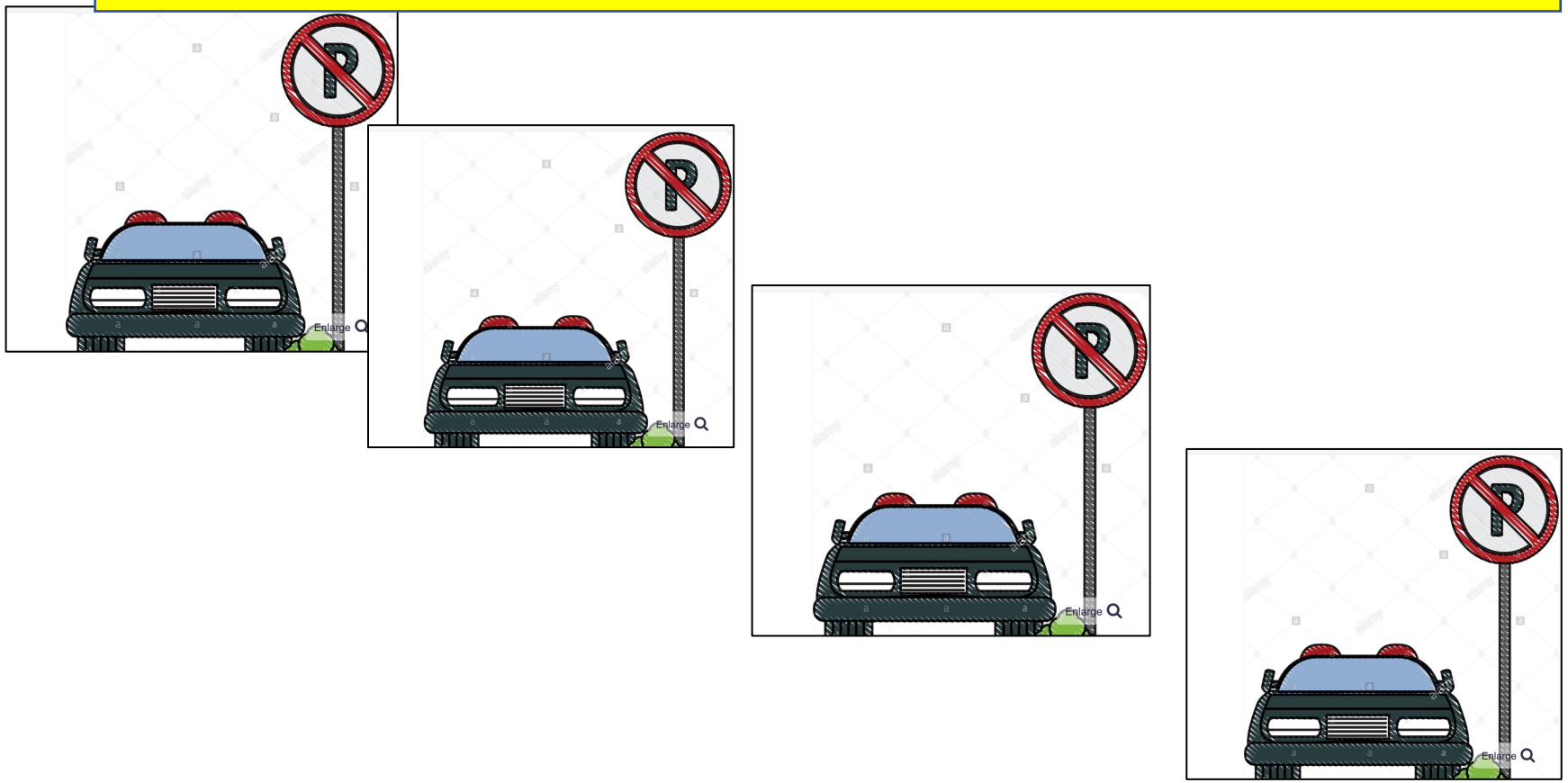

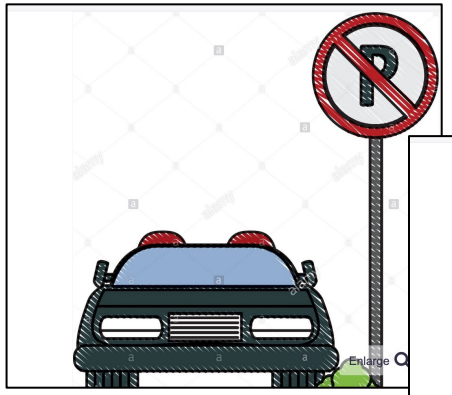
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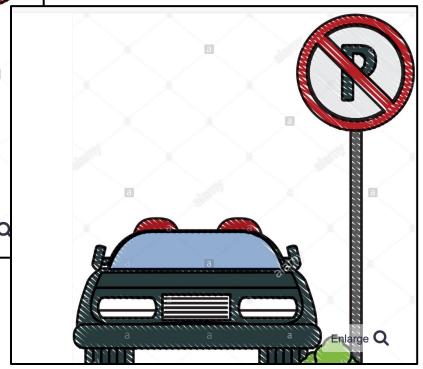
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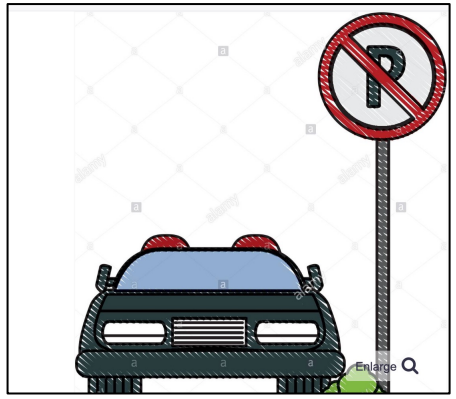
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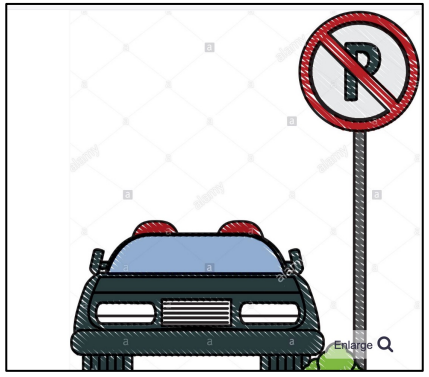
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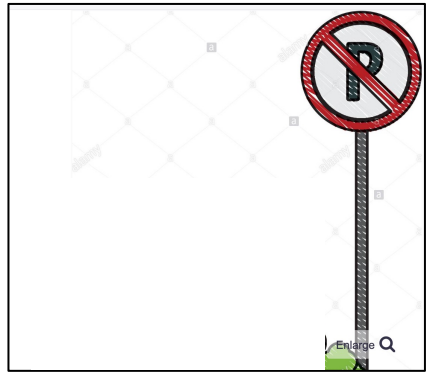
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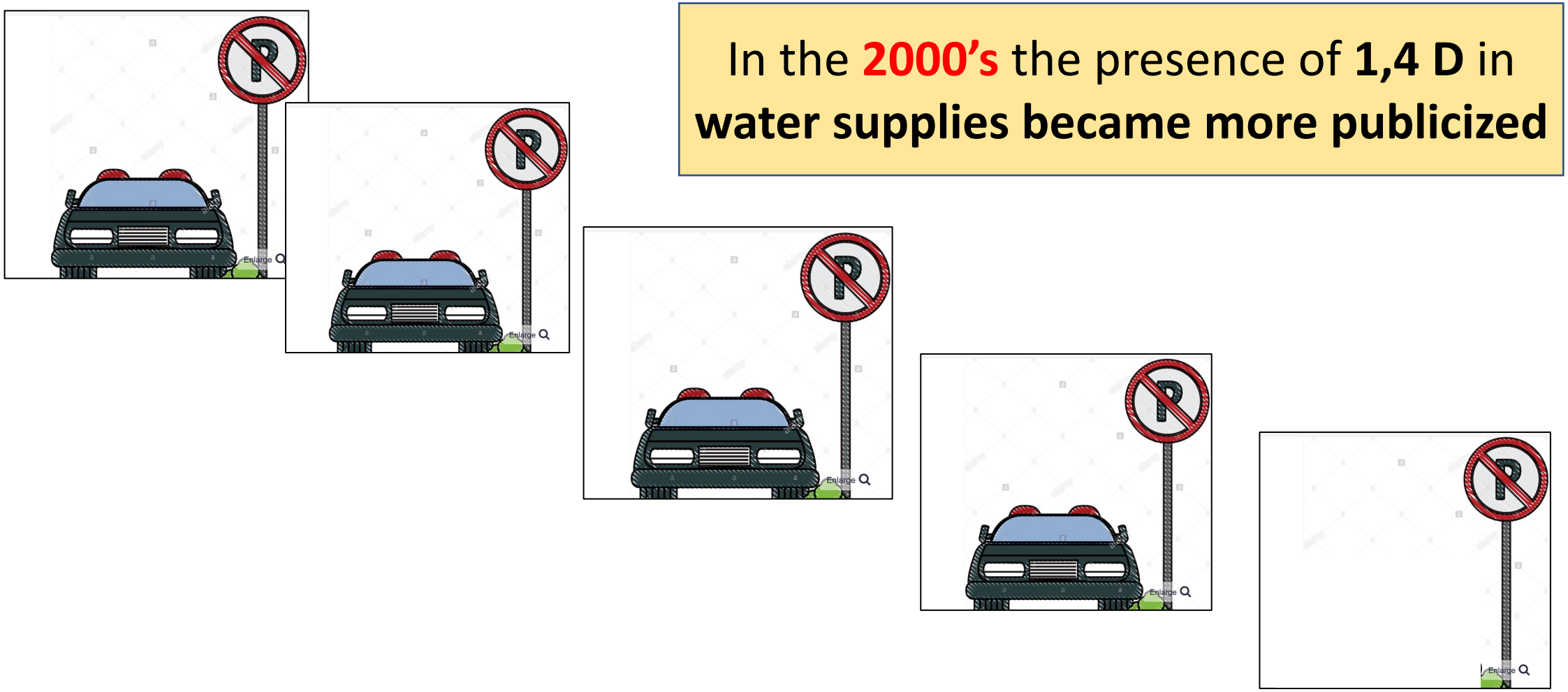
In the **2000's** the presence of **1,4 D** in **water supplies became more publicized**



The lack of response of the industry to reducing 1,4 D in cleansing products gave an opening to alternative organizations to ”control the conversation”

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Environmental Working Group

Corporation

ewg

Environmental Working Group
Corporation

ewg

2007

Cancer-causing Chemical Found in Children's Bath Products

Women's Shampoos and Body Wash also Contaminated

Environmental Working Group
Corporation

ewg

2007

Product	1,4 Dioxane
Baby & Children's Consumer Products	
Disney Clean as Can Bee Hair & Body Wash (Water Jel Technologies)	8.8 ppm
Disney Pixar Cars Piston Cup Bubble Bath (MZB Personal Care)	2.2 ppm
Gerber Grins & Giggles Gentle & Mild Aloe Vera Baby Shampoo	8.4 ppm
Hello Kitty Bubble Bath (Kid Care)	12 ppm*
Huggies Baby Wash Shea Butter	4.0 ppm
Huggies Natural Care Baby Wash Extra Gentle and Tear Free	4.2 ppm
Johnson's Head-to-Toe Baby Wash (Johnson & Johnson)	5.3 ppm to 6.1 ppm
Johnson's Kids Tigger Bath Bubbles (Johnson & Johnson)	5.6 ppm to 7.9 ppm
Johnson's Kids Shampoo Watermelon Explosion (Johnson & Johnson)	10 ppm*
Lil' Bratz Mild Bubble Bath (Kid Care)	3.7 ppm
L'Oreal Kids Orange Mango Smoothie Shampoo	2.0 ppm
Mr. Bubble Bubble Bath Gentle Formula with Aloe	1.5 ppm
Rite-Aid Tearless Baby Shampoo	4.3 ppm
Scooby-Doo Mild Bubble Bath (Kid Care)	3.0 ppm
Sesame Street Wet Wild Watermelon Bubble Bath (The Village Company)	7.4 ppm
Adult Consumer Products	
Clairol Herbal Essences Rainforest Flowers Shampoo	23 ppm*
Olay Complete Body Wash with Vitamins (normal skin)	23 ppm*
Suave Naturals Passion Flower	2.0 ppm

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Corporation

Soon, the issue of 1,4 D was expanded to any other cosmetic product…

Environmental Working Group Corporation

ewg

“ To avoid 1,4-dioxane, avoid cosmetics with sodium laureth sulfate and ingredients that include "PEG," "xynol," "ceteareth," and "oleth.”

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ewg

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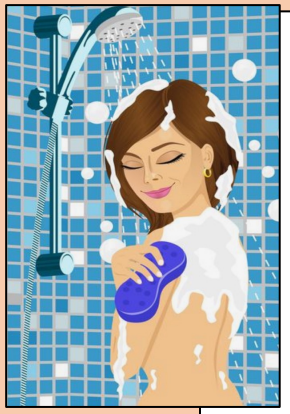
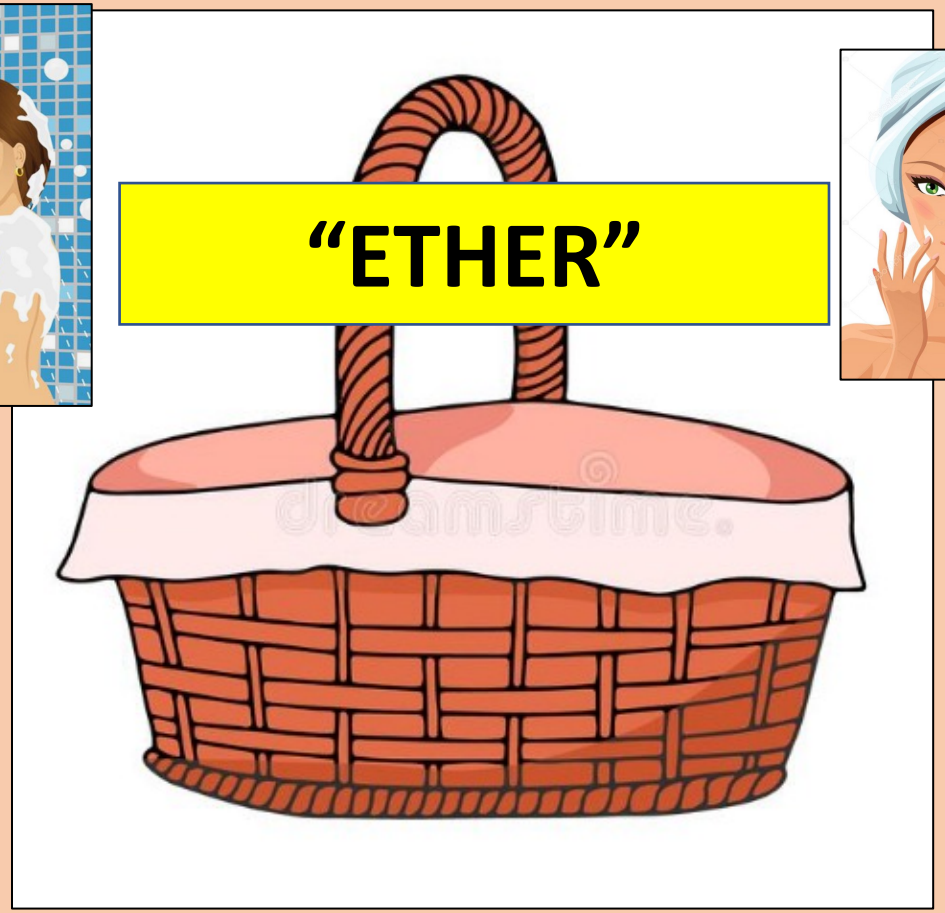
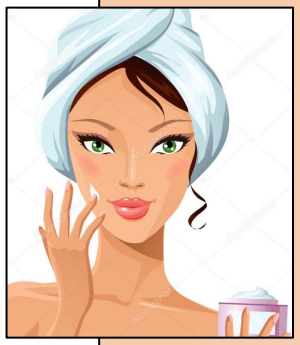




“ETHER”



2007

EWG Research Shows 22 Percent of All Cosmetics May Be Contaminated With Cancer-Causing Impurity 1,4 Dioxane

“ Using a new, computerized assessment of ingredients”

which means…

Environmental Working Group

Corporation

Today's Skin Deep® Numbers:

73,886 Products

2,526 Brands

1,882 EWG Verified™ Products

Environmental Working Group
Corporation

ewg

Today's Skin Deep® Numbers:

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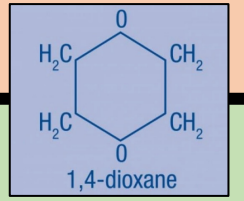
have the **potential to have 1,4 D**



How BAD is this chemical ?

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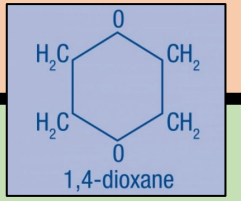

How BAD is this chemical ?

Environmental Working Group

Corporation

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Environmental Working Group

Corporation

ewg

CAMPAIGN for SAFE COSMETICS

Alternative Facts

“DRAMATIC EFFECTS”

Environmental Working Group

Corporation

ewg

1st - Alternative Fact

1,4-D approached as **industrial solvent**

Environmental Working Group

Corporation

ewg

NEWS & INSIGHTS / OUR EXPERTS

Thomas Galligan, Ph.D.

Toxicologist

AREAS OF FOCUS

Personal Care Products
Cleaning Supplies
Pesticides

PRESS CONTACT

monica@ewg.org
(202) 939-9140

Totally disregarding….

“Only the dose makes the poison”

Ingestion

Dermal

Inhalation

- **Paracelsus (1493-1541)**

2nd Alternative Fact

MYTH vs. FACT 1,4-Dioxane (Diethylene Oxide) and Cosmetic Safety

ADOPTED FROM THE CAMPAIGN FOR SAFE COSMETICS

MYTH ▸ A SMALL AMOUNT OF A CHEMICAL CARCINOGEN IN A PERSONAL CARE PRODUCT ISN'T DANGEROUS

FACTS ▾

- When laboratory animals were tested with 1,4-Dioxane at the lowest parts per billion level—over the animal's lifetime—they developed cancer. [1], [2]
- The levels of 1,4-Dioxane found in many personal care products are 1,000 times higher than those found to cause cancer in laboratory animals. Based on this fact, these should not be considered "low levels" of 1,4-Dioxane. [3]
- The combined effects of lifetime exposure to 1,4-Dioxane and other carcinogens can create synergistic effects, so that levels from multiple compounds add up and even multiply to create greater risk. [3]

MYTH ▸ ANIMAL STUDIES ARE IRRELEVANT TO IDENTIFYING PROBABLE HUMAN CARCINOGENS

FACTS ▾

- Because we cannot ethically test carcinogens on a human population, the World Health Organization and most domestic & international regulatory bodies have advised that chemicals that are found to induce cancer in rodents should be considered to cause cancer in humans. [4]
- "It is also noteworthy that all known carcinogenic agents for man have been shown to be also carcinogenic in animals and frequently in the same site. Hence, common pathogenetic factors are clearly involved in the development of cancer in man and in animals." -Roy Hertz, M.D., PH.D., of the National Institutes of Health. [5], [6]

MYTH ▸ 1,4-DIOXANE'S TOXICITY IS QUESTIONABLE

FACTS ▾

- US federal regulation systems (specifically, the Integrated Risk Information System) consider dioxane's potency to be equivalent or greater than many pesticides considered to be dangerous to human health. [8]
- The Environmental Protection Agency classifies 1,4-Dioxane as a "Group B2, probable human carcinogen," based on "induction of nasal cavity and liver carcinomas in multiple strains of rats, liver carcinomas in mice, and gall bladder carcinomas in guinea pigs." [1]
- The State of California's EPA lists 1,4-Dioxane on its publicly mandated annual list of chemicals known to cause cancer or reproductive toxicity. [9]
- According to the New Jersey Department of Health and Senior Services 1,4-Dioxane "should be handled as a **Carcinogen—With Extreme Caution.**" [10]
- In federally funded National Toxicology Program studies, the chemical has induced cancer in both sexes of rats and both sexes of mice. [2]
- "There is sufficient evidence for the carcinogenicity of 1,4-Dioxane in experimental animals," notes the most recent Eleventh Annual Report on Carcinogens, published by the US Department of Health and Human Services, National Toxicology Program, which lists chemicals reasonably anticipated to cause human cancer. [11]
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EPA United States Environmental Protection Agency

Technical Fact Sheet – 1,4-Dioxane

November 2017

TECHNICAL FACT SHEET – 1,4-DIOXANE

"This fact sheet is intended for use by **site managers** who may address **1,4-dioxane at cleanup sites or in drinking water supplies** and for those in a position to consider whether 1,4-dioxane should be added to the analytical suite for site investigations"

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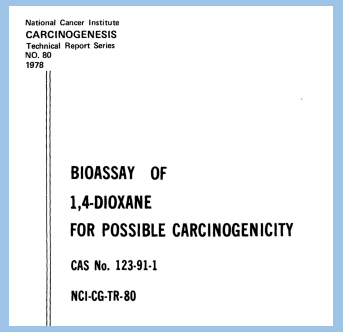
National Cancer Institute
CARCINOGENESIS
Technical Report Series
NO. 80
1978

BIOASSAY OF
1,4-DIOXANE
FOR POSSIBLE CARCINOGENICITY

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NCI-CG-TR-80

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NO. 80
1978

BIOASSAY OF 1,4-DIOXANE FOR POSSIBLE CARCINOGENICITY

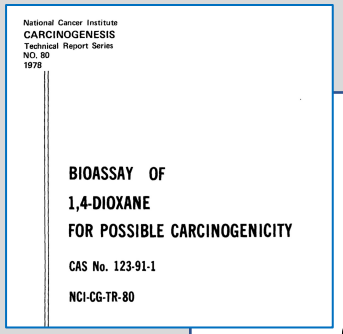
CAS No. 123-91-1

NCI-CG-TR-80

Context: Industrial solvent

1,4 D

1,4-Dioxane (CAS 123-91-1; NCI C03689), a dimer of ethylene oxide, hereinafter called dioxane, is used extensively as an industrial solvent for lacquers, varnishes, paints, plastics, dyes, oils, waxes, resins, and cellulose acetate and as an inhibitor in chlorinated solvents (Stecher, 1968; Stanford Research Institute, 1975; Matheson, 1972). In biological and chemical laboratories, dioxane is employed as a solvent for tissue processing, liquid scintillation counting, and photochemical reactions. Nearly 18 million pounds were produced for these uses in 1973 (U. S. International Trade Commission, 1976).

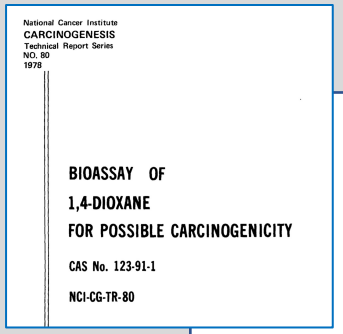


Context:
Industrial solvent

1,4 D

"Daily administration

caused pronounced toxic effects
including the occurrence of hepatic and nasal tumors"


National Cancer Institute
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1978

BIOASSAY OF
1,4-DIOXANE
FOR POSSIBLE CARCINOGENICITY

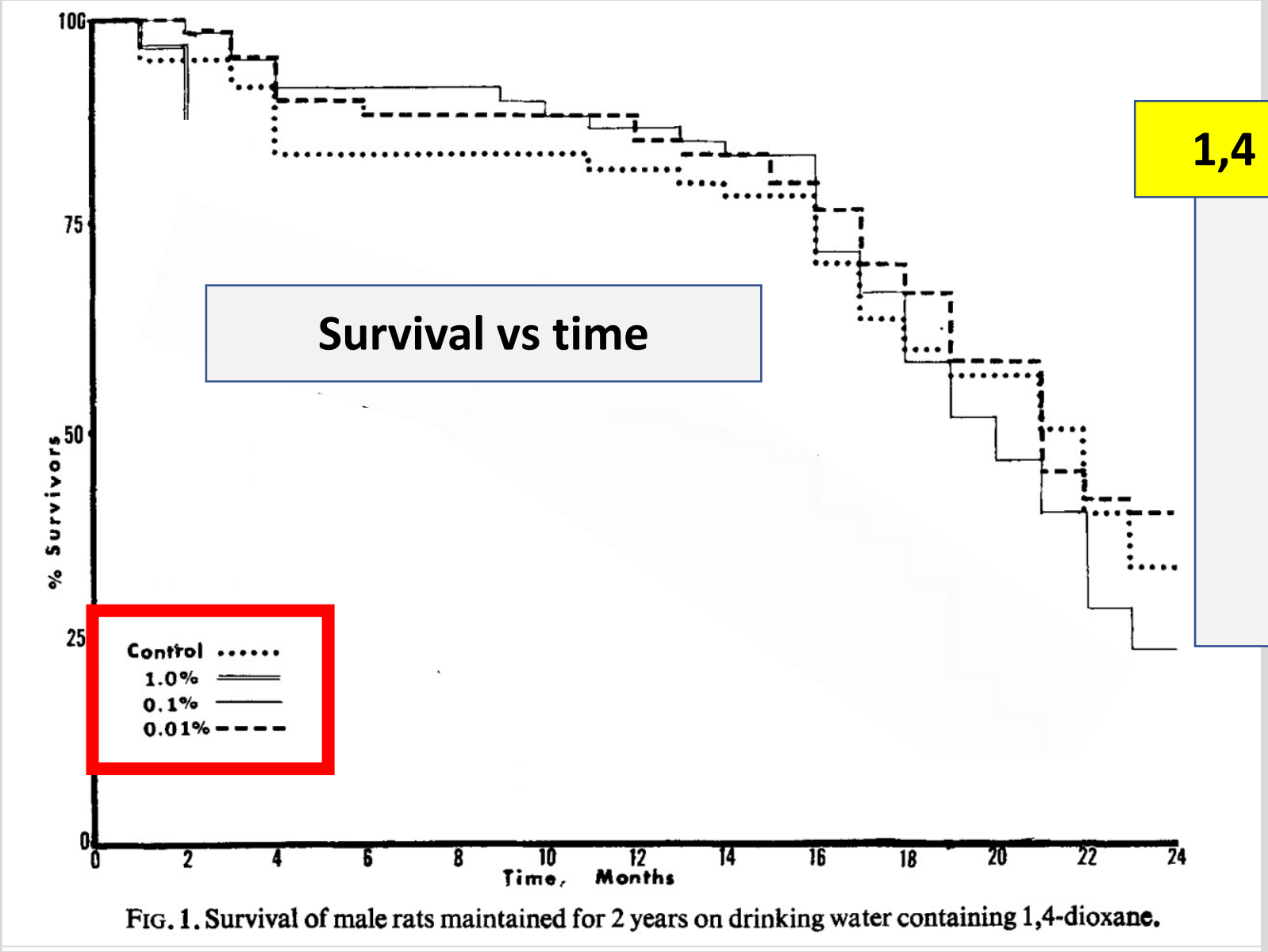
CAS No. 123-91-1

NCI-CG-TR-80

Context:
Industrial solvent

1,4 D

"Daily administration of **massive toxic doses**
(1.0% in drinking water)
for up **to 2 years** caused pronounced toxic effects
including the occurrence of hepatic and nasal tumors"



Survival vs time

1,4 D added to water

Control
vs
0.01 %
and
0.1%

FIG. 1. Survival of male rats maintained for 2 years on drinking water containing 1,4-dioxane.

"Only the dose makes the poison"

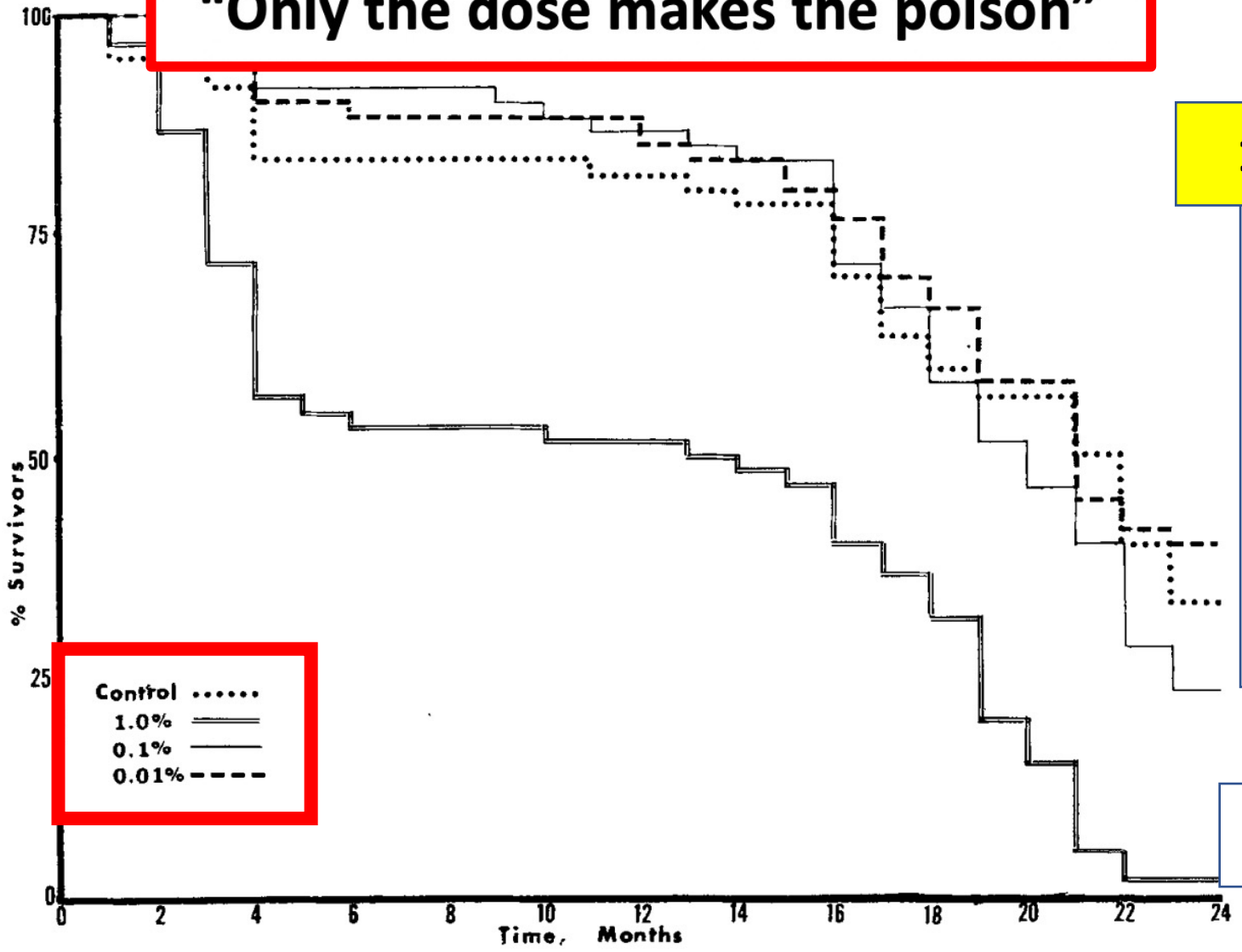


FIG. 1. Survival of male rats maintained for 2 years on drinking water containing 1,4-dioxane.

1,4 D added to water

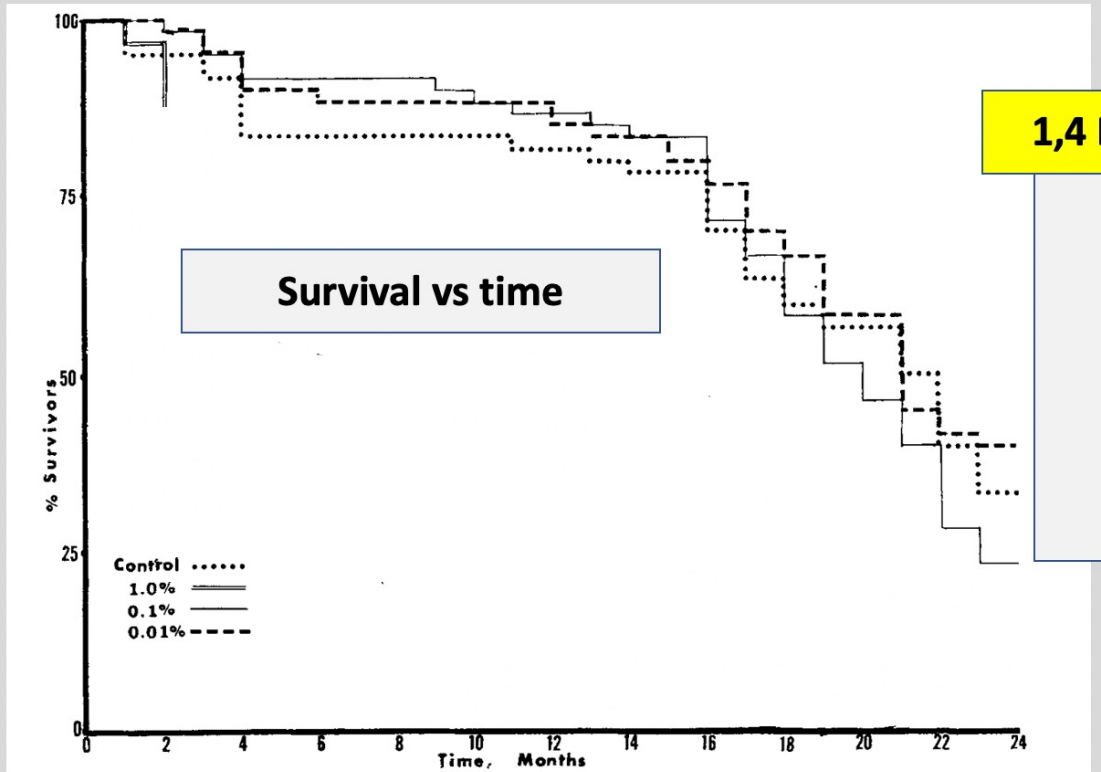
Control
vs
0.01 %
and
0.1%

Effect at 1%

Fine tuning between 0 %, 0.5 % and 1 %

	Initial No. of Animals[a]	1,4-Dioxane in Drinking Water (%,v/v)	Average Dose (mg/kg/day)[b]
Matched-Control[c]	35	0	0
Low-Dose	35	0.5	240(130-380)
High-Dose[c]	35	1.0	530(290-780)

When laboratory animals were tested with 1,4-Dioxane at the lowest parts per billion level—over the animal's life-time—they developed cancer. [1], [2]



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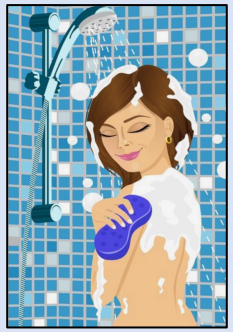
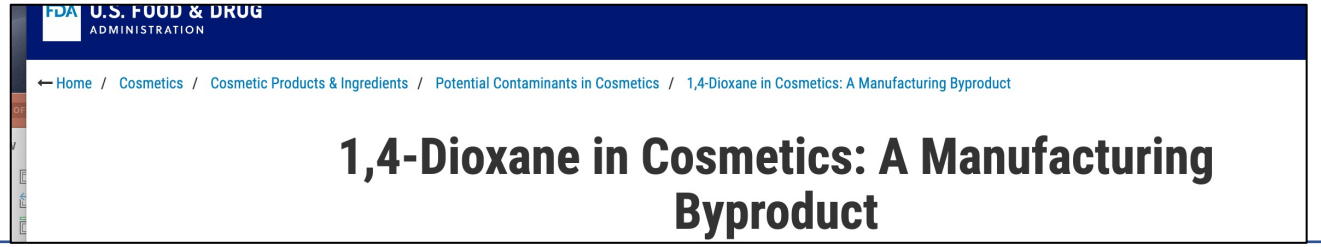
CAMPAIGN for SAFE COSMETICS



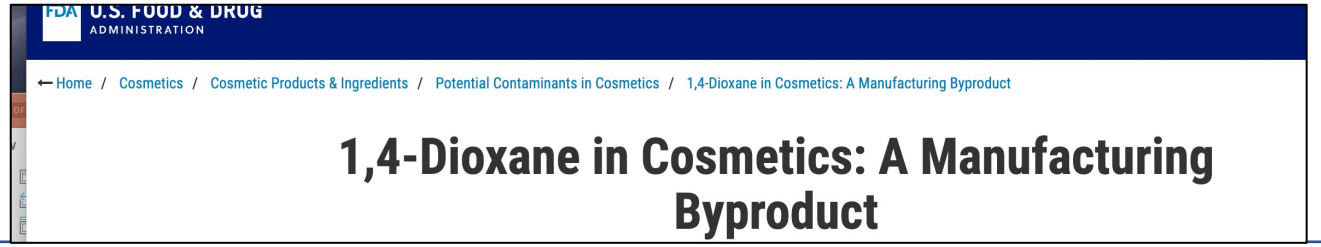
The FDA has stated that, "Skin absorption studies demonstrated that dioxane readily penetrates animal and human skin from various types of vehicles."

For example, during exposure to 1,4-Dioxane from a bath product, a person's skin is warmed, pores are opened, the skin is soaked in the contaminated water, and 1,4-Dioxane enters the bloodstream.



readily penetrates

CAMPAIGN for SAFE COSMETICS

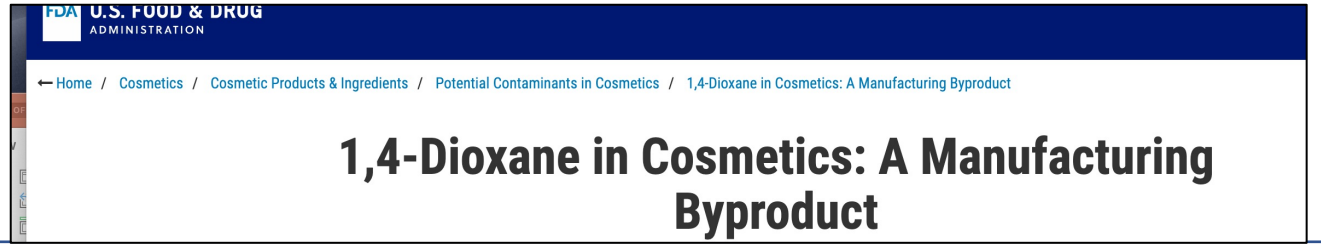


The FDA also conducted skin absorption studies of 1,4 D, which showed it

can penetrate animal and human skin when applied in certain preparations, such as lotions.

readily penetrates

CAMPAIGN for SAFE COSMETICS



The FDA also conducted skin absorption studies of 1,4 D, which showed it **can penetrate** animal and human skin when applied in certain preparations, such as lotions.

However, further research by the FDA determined that **1,4-dioxane evaporates readily,** diminishing the already small amount available for skin absorption, even in products that remain on the skin for hours [3].

CAMPAIGN for SAFE COSMETICS

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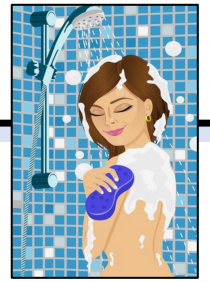

Ignorance ?
Malice ?

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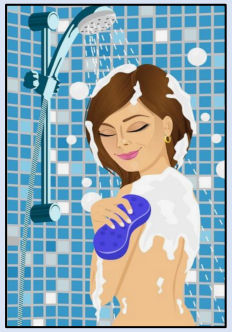
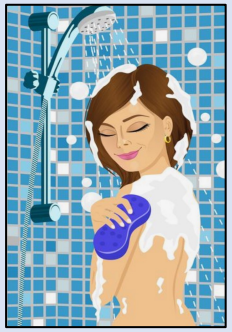
CAMPAIGN for SAFE COSMETICS



CAMPAIGN for SAFE COSMETICS



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For example, during exposure to 1,4-Dioxane from a bath product, a person's skin is warmed, pores are opened, the skin is soaked in the contaminated water, and 1,4-Dioxane enters the bloodstream. 1,4-Dioxane is also released as a gas and is inhaled as it is trapped in the enclosed area of the bathroom or shower.

“Only the dose makes the poison”

Ingestion

Dermal

Inhalation

Paracelsus
(1493-1541)

As Industrial Solvent

TOXICOLOGY AND APPLIED PHARMACOLOGY 30, 287–298 (1974)

1974

Inhalation

1,4-Dioxane. II. Results of a 2-Year Inhalation Study in Rats

T. R. TORKELSON, B. K. J. LEONG, R. J. KOCIBA, W. A. RICHTER,[1] AND P. J. GEHRING

Toxicology Unit, Health and Environmental Research, The Dow Chemical Company, Midland, Michigan 48640 and the Department of Pathology, University of Chicago, Chicago, Illinois

Received January 4, 1974; accepted May 8, 1974

2 years at
1.4 ppm in air

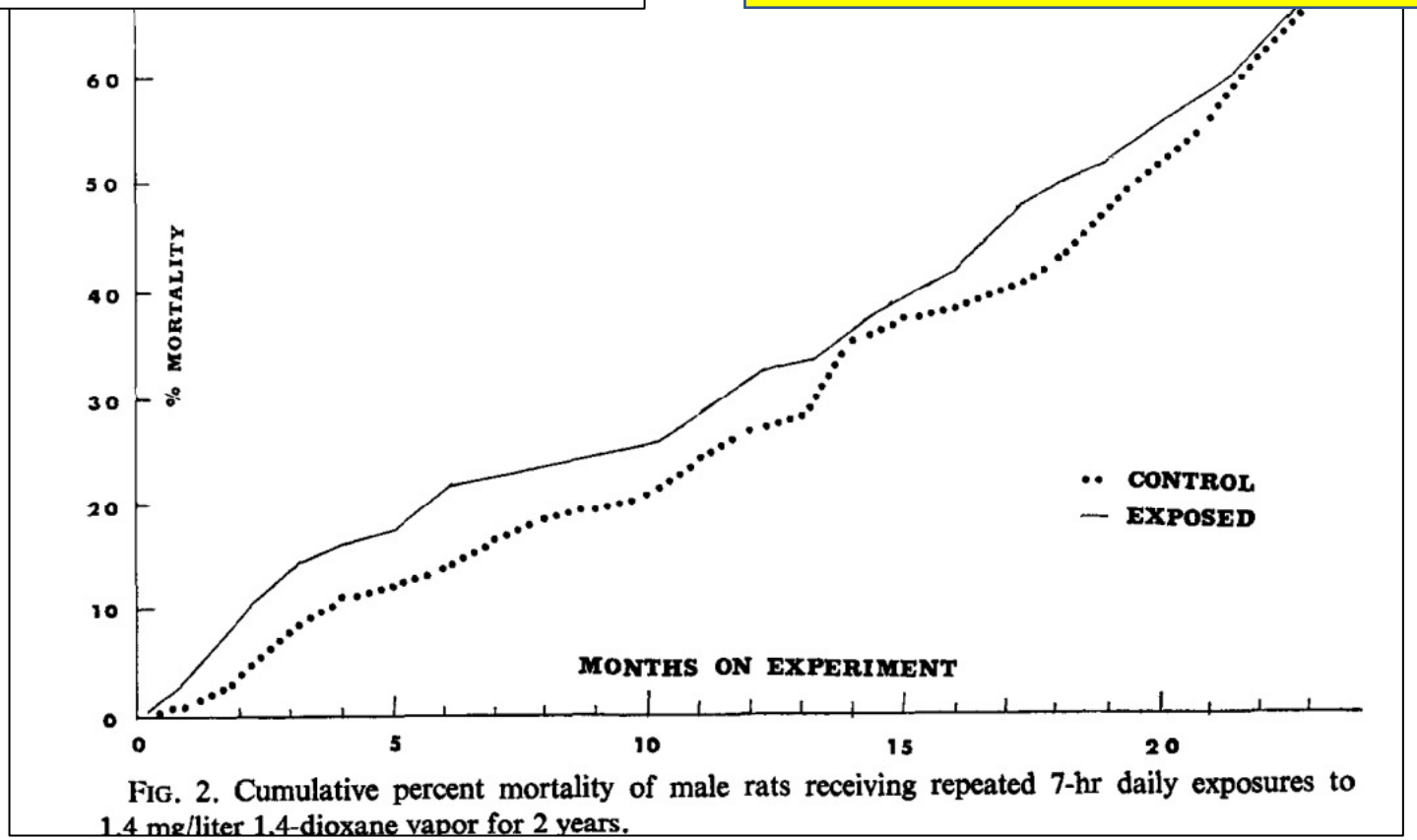


FIG. 2. Cumulative percent mortality of male rats receiving repeated 7-hr daily exposures to 1.4 mg/liter 1,4-dioxane vapor for 2 years.

2008

Research Article

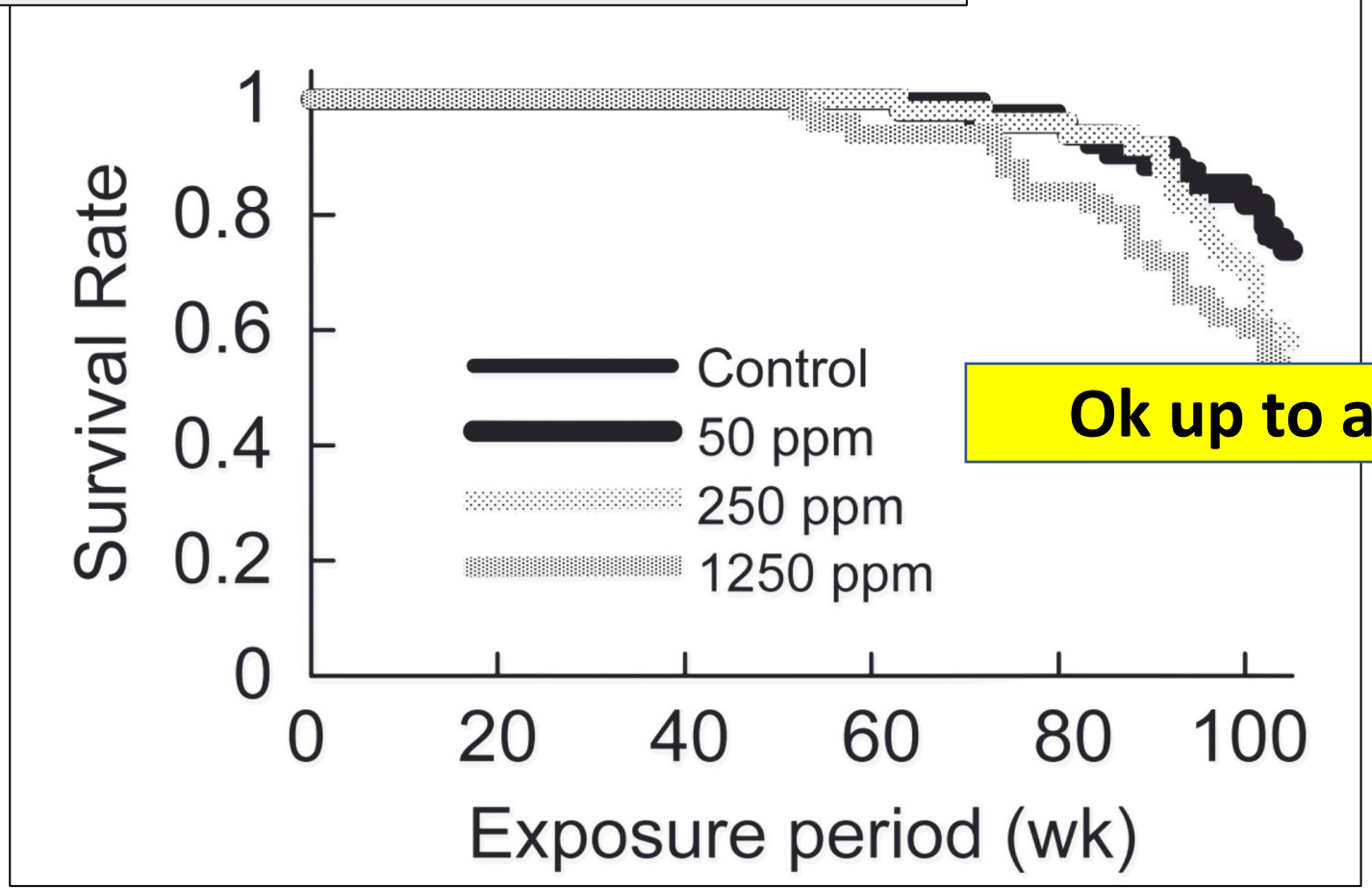
Two-year inhalation study of carcinogenicity and chronic toxicity of 1,4-dioxane in male rats

Tatsuya Kasai, Hirokazu Kano, Yumi Umeda, Toshiaki Sasaki, Naoki Ikawa, Tomoshi Nishizawa, ...show all

Pages 889-897 | Received 01 Oct 2008, Accepted 17 Nov 2008, Published online: 17 Aug 2009

Download citation https://doi-org.proxy.libraries.rutgers.edu/10.1080/08958370802629610

2 years Inhalation at 0, 50, 250 and to 1250 ppm



Ok up to at least 50 ppm

EPA United States Environmental Protection Agency

Technical Fact Sheet – 1,4-Dioxane
November 2017

TECHNICAL FACT SHEET – 1,4-DIOXANE

INHALATION

EPA has calculated **a residential air screening level** of 0.56 micrograms per cubic meter (µg/m3) **130 ppb**

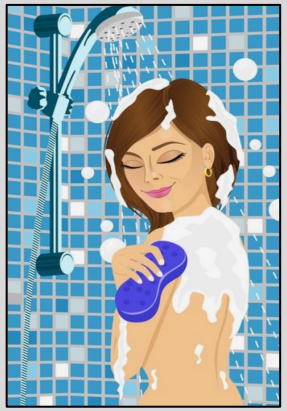
Screening Assessment for the Challenge

1,4-Dioxane

Chemical Abstracts Service Registry Number
123-91-1

Health Canada

Environment Canada
Health Canada



Screening Assessment for the Challenge

1,4-Dioxane

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Environment Canada
Health Canada

THEORETICAL CASE STUDY

Inhalation

Dermal

Consumer product scenario	Assumptions	Estimated exposure
Skin moisturizer (body cream)	**Inhalation (constant rate)** - Concentration: 0.0075 % (VCCEP 2007) - Used ConsExpo model version 4.1, exposure to vapour, constant release mode[1] - Frequency: 730 times/year[1] - Body weight: 70.9 kg, adult - Limited air concentration to vapour pressure of pure substance - Exposure duration: 12 h[1] - Room volume: 20 m^3 [1] - Ventilation rate: 1/h[1] - Applied amount: 8 g (90% partitioning, model input 7.2 g)[1] - Release duration: 20 min[2] - Inhalation rate: 36.7 m^3/day[1] - Uptake fraction: 1	Mean event concentration = 2.25×10^{-3} mg/m^3 Chronic dose = 1.16×10^{-3} mg/kg-bw per day
	Dermal (direct dermal contact with product: instant application) - Concentration: 0.0075 % (VCCEP 2007) - Exposed area: 1.63×10^4 cm^2 [1] - Applied amount: 8 g (10% partitioning, model input 0.8 g)[1] - Uptake fraction: 1 - Skin retention factor: 1	Chronic dose = 1.69×10^{-3} mg/kg-bw per day

”The resulting margins of exposure are approximately 8000–13300 ”

Screening Assessment for the Challenge

1,4-Dioxane

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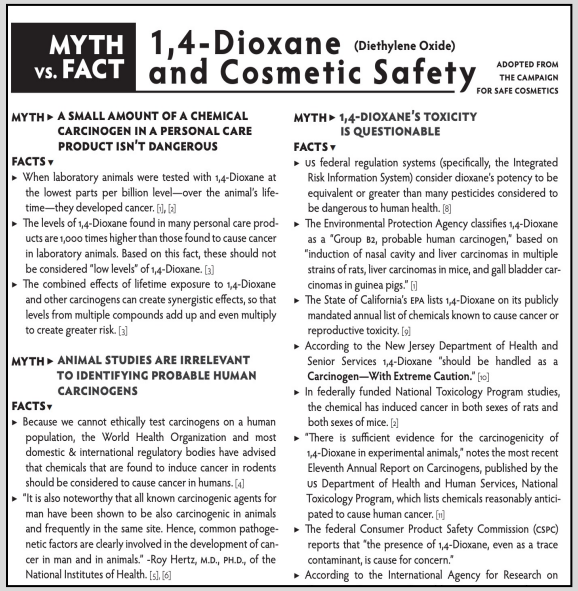
Health Canada

Environment Canada
Health Canada



MYTH vs. FACT

1,4-Dioxane (Diethylene Oxide) and Cosmetic Safety

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CAMPAIGN for SAFE COSMETICS

Misinformation

Misquotations

Speculations

Environmental Working Group

Corporation

ewg

CAMPAIGN for SAFE COSMETICS

1- Alternative Facts

2- “DRAMATIC EFFECTS”

2019

Environmental Working Group Corporation

ewg

Johnson's Baby Shampoo	0.87 pm
Garnier Fructis with Active Fruit Protein	0.4 ppm
Olay Moisture Ribbons Plus Body Wash	3.5 ppm
Dove Nutritive Solutions (Coconut and Hydration)	2.2 ppm

Environmental Working Group Corporation

ewg

"DRAMATIC EFFECTS"

	ppb
Johnson's Baby Shampoo	870
Garnier Fructis with Active Fruit Protein	400
Olay Moisture Ribbons Plus Body Wash	3,500
Dove Nutritive Solutions (Coconut and Hydration)	2,200

“DRAMATIC EFFECTS”

CAMPAIGN for SAFE COSMETICS

Cosmetics: An industry of death

Based on the presence of dioxane in common ingredients o
cosmetic ingredients may contain harmful impurities linked

Environmental Working Group Corporation

ewg

CAMPAIGN for SAFE COSMETICS

Misquotations

Misinformation

Speculations

The response of the cosmetic industry to all this ?

The response of the cosmetic industry to all this ?

Environmental Working Group Corporation

ewg

CAMPAIGN for SAFE COSMETICS

Misquotations

Misinformation

Speculations

Some sectors use it as Marketing Tool !!!

Concerns over **alkyl sulfates** and **alkyl ether sulfates** in personal cleansers started >10 years ago as a small fringe and an internet blog.

innospec

Concerns over **alkyl sulfates** and **alkyl ether sulfates** in personal cleansers started >10 years ago as a small fringe and an internet blog.

Consumer Perception of Sulfate-Free Products

- **Milder to skin and hair than ordinary shampoo, body washes, or personal cleansers.**
- **Pure - which equates to "safer" for the consumer.**
- **Non Stripping and give gentler cleansing.**
- **Natural/Organic – more environmentally friendly.**
- **Better for sensitive skin.**

innospec

And finally….

c&en
CHEMICAL & ENGINEERING NEWS

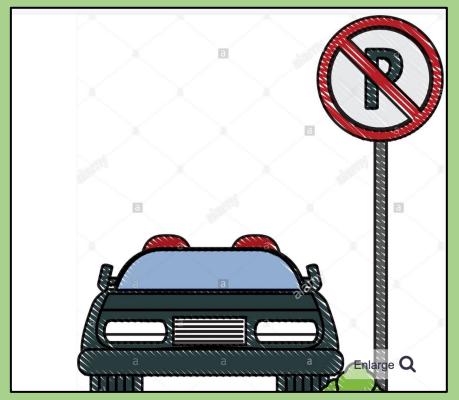
PERSISTENT POLLUTANTS

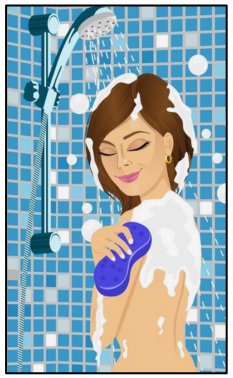
New York restricts 1,4-dioxane in cleaning and personal care products

State is first in US to limit level of this persistent pollutant in consumer goods

by **Cheryl Hogue**

DECEMBER 13, 2019





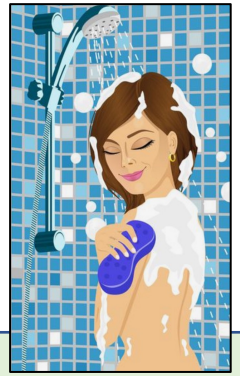
Rinse-off

- End 2022: 2 ppm
- End 2023: 1 ppm

1, 4 Dioxane

Leave-on

End 2022: 10 ppm.



Rinse-off

- End 2022: 2 ppm
- End 2023: 1 ppm

Why the difference ?

1, 4 Dioxane

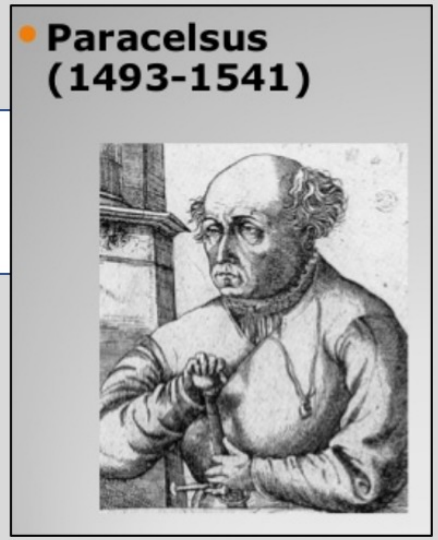
Leave-on

End 2022: 10 ppm.

Why ?

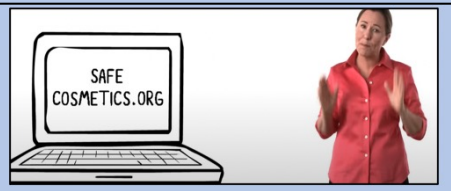
"Only the dose makes the poison"

- Ingestion
- Dermal
- Inhalation



Why ?

Environmental Working Group
Corporation



EWG Research Shows 22 Percent of All Cosmetics May Be Contaminated With Cancer-Causing Impurity

1,4-D was treated under the same conditions of usage as an industrial solvent

Scientific Committee on Consumer Safety

SCCS

2015

SCIENTIFIC OPINION ON

The Report of the ICCR Working Group: Considerations on Acceptable Trace Level of 1,4-Dioxane in Cosmetic Products

The SCCS adopted this Opinion at its 12th Plenary meeting

on 15 December 2015

2017

Traces/1,4-Dioxane Report/Final-January 2017

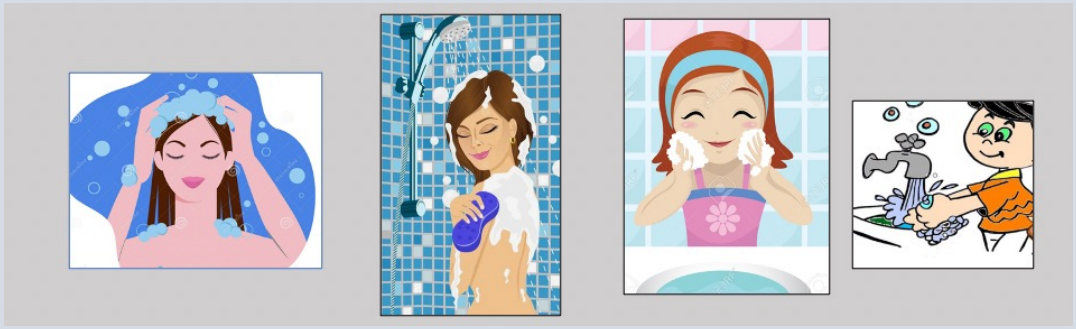
INTERNATIONAL COOPERATION ON COSMETICS REGULATION

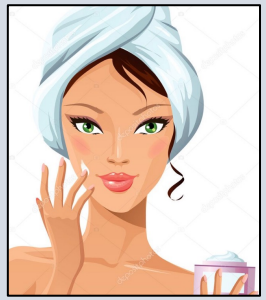
ICCR, an international group of regulatory authorities from the United States, the European Union, Japan, Canada, and Brazil), and by the European Commission Scientific Committee on Consumer Safety (SCCS)), have examined this issue…

..and determined that all of the levels of 1,4 D reported in the recent literature are within acceptable margins of exposure based on available safety assessments from Canada, Europe, and Japan [1].

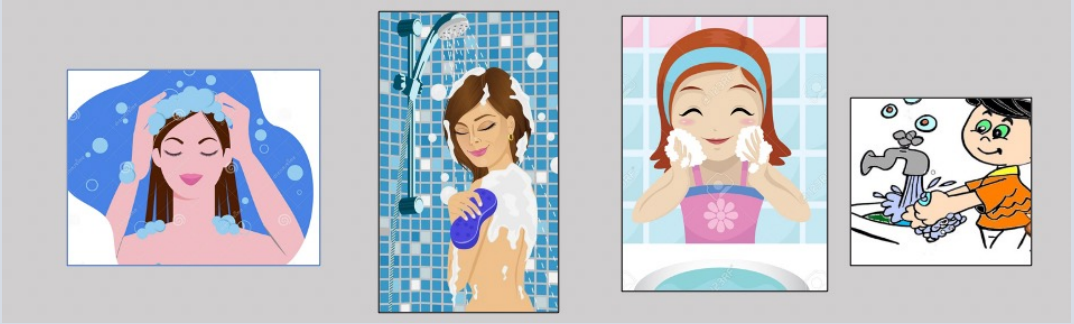
In an independent risk assessment, SCCS concluded that products with

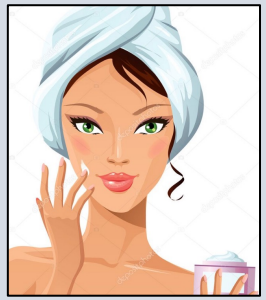
≤10 ppm of 1,4 D are considered safe[2].





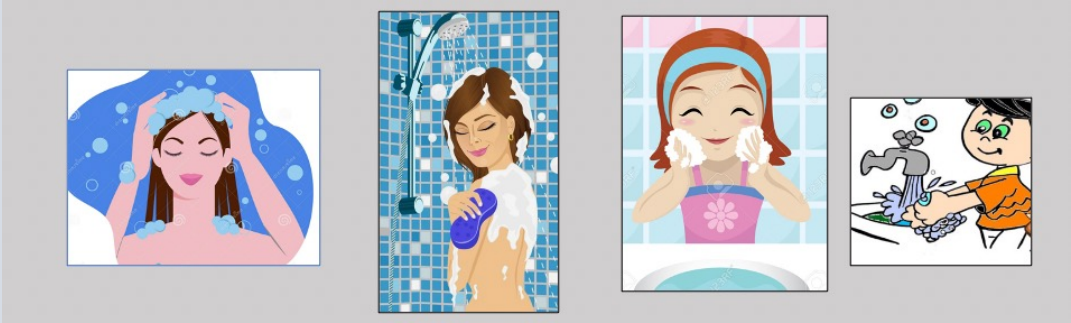
10 ppm max 1,4 D

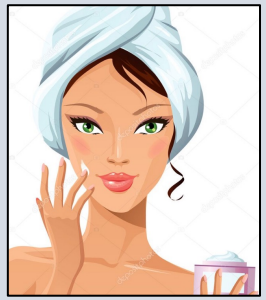




10 ppm max 1,4 D

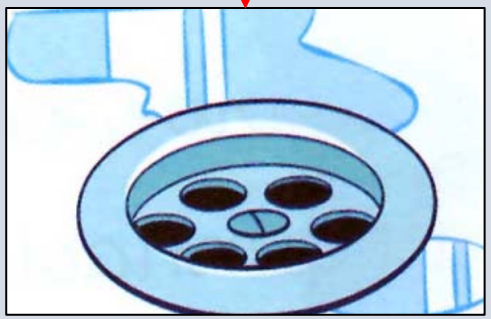
BUT…..

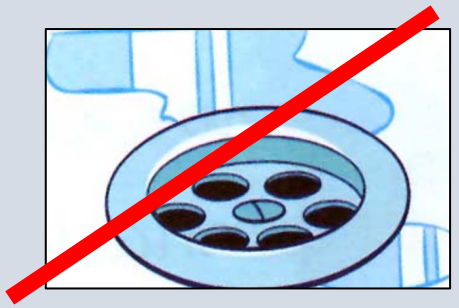




1,4 D

1,4 D





Real issue IS…

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Current Opinion in Environmental Science

NC STATE UNIVERSITY

1,4-Dioxane in drinking water: emerging for 40 years and still unregulated

Amie C. McElroy[1], Michael R. Hyman[2] and Detlef R. U. Knappe[1]

Abstract
The likely human carcinogen 1,4-dioxane was first detected in drinking water more than 40 years ago, and a recent analysis suggests that almost 30 million people in the United States receive drinking water with 1,4-dioxane levels above the health-based reference concentration of 0.35 μg/L. The widespread occurrence of 1,4-dioxane has exposed the need for developing and implementing management and treatment approaches that protect drinking water sources and prevent human exposure to 1,4-dioxane through drinking water. In this review, we highlight recent advances in analytical methods, understanding of occurrence, and treatment processes. Findings are discussed in the context of managing 1,4-dioxane as a drinking water contaminant, and recommendations are made to address important knowledge gaps.

Addresses
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Current Opinion in Environmental Science & Health 2019, **7**:117–125

This review comes from a themed issue on **Drinking water contaminants**

Edited by **Susan Richardson** and **Cristina Postigo**

For a complete overview see the Issue and the Editorial

https://doi.org/10.1016/j.coesh.2019.01.003

Keywords
Adsorption, Biodegradation, Mass spectrometry, Oxidation, Source water protection.

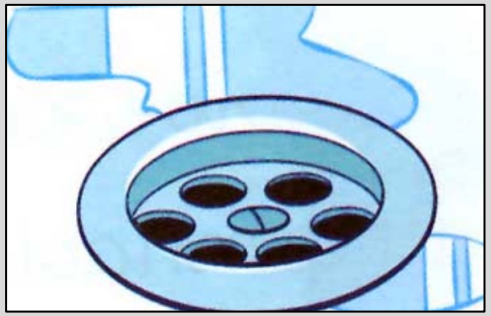
Introduction

1,4-Dioxane, a cyclic diether, is a synthetic organic chemical with widespread impact on drinking water sources around the globe [1–5]. In the United States (US), it is a known drinking water contaminant since at least 1978 [6]. Despite the early awareness, it continues to be considered a contaminant of emerging concern that is drinking water relevant [7]. Concerns include (1) its classification as a likely human carcinogen by all routes of exposure [8], (2) the absence of enforceable drinking water standards in many countries, and (3) the inability of many widely used water treatment processes to control 1,4-dioxane [2]. 1,4-Dioxane is miscible in water, essentially nonvolatile when dissolved in water, not well adsorbed by activated carbon, not readily oxidized by common oxidants, and not readily biodegraded at concentrations relevant to drinking water [5,9].

In the US, 1,4-dioxane has received increased attention as a drinking water contaminant since its inclusion on the US Environmental Protection Agency's (USEPA's) Third and Fourth Contaminant Candidate Lists and on the analyte list of USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR3). Also, in December 2016, the USEPA included 1,4-dioxane on a list of 10 chemicals that are subject to the agency's initial chemical risk evaluations as required by the Toxic Substances Control Act [5,10]. Furthermore, recent findings of widespread occurrence of 1,4-dioxane in US drinking water [1] have highlighted the need to develop and implement effective management and treatment approaches that protect drinking water sources and reduce human exposure to 1,4-dioxane via drinking water. The goal of this review is to (1) summarize recent advances in analytical methods, understanding of occurrence, and treatment approaches, (2) discuss findings in a context of managing 1,4-dioxane as a drinking water contaminant, and (3) make recommendations for addressing key knowledge gaps.

Health-based reference concentrations

Human exposure to 1,4-dioxane through drinking water can occur by ingestion, inhalation, and dermal contact [11]. Based on available toxicological data, the USEPA derived an oral cancer slope factor of 0.01 $(mg/kg\text{-}day)^{-1}$ for 1,4-dioxane. Health-based reference values for 1,4-dioxane have been calculated for 10^{-6}, 10^{-5}, and 10^{-4} excess lifetime cancer risks and correspond to drinking water concentrations of 0.35, 3.5, and 35 μg/L, respectively [8,12]. The noncancer reference dose of 0.03 mg/kg-day is based on chronic liver and kidney toxicity [8,12]. Even though the volatility of aqueous 1,4-dioxane is low at room temperature, its volatility increases with increasing temperature such that inhalation exposure can be important during activities involving hot water, such as taking showers or baths [13]. For inhalation, the cancer unit risk is 5×10^{-6} $(\mu g/m^3)^{-1}$,



Contents lists ava
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Stony Brook University

1,4-Dioxane drinking water occurrence data from the third unregulated contaminant monitoring rule

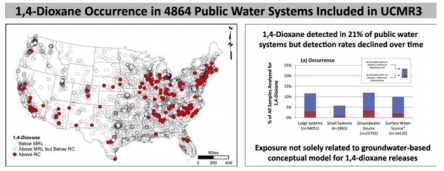
David T. Adamson [a,*], Elizabeth A. Piña [a], Abigail E. Cartwright [b], Sharon R. Rauch [a], R. Hunter Anderson [c], Thomas Mohr [d], John A. Connor [a]

[a] GSI Environmental Inc., Houston, TX 77098, USA
[b] Rice University, 6100 Main Street, Houston, TX 77005, USA
[c] Air Force Civil Engineer Center, San Antonio, TX 78226, USA
[d] Santa Clara Valley Water District, 5750 Almaden Expressway, San Jose, CA 95118, USA

HIGHLIGHTS

- 1,4-Dioxane and other unregulated contaminants in drinking water were evaluated.
- 1,4-Dioxane exhibited relatively high rates of detection in public water systems.
- 1,4-Dioxane did not follow common assumptions about release and exposure routes.
- Regulatory determinations on 1,4-dioxane will have significant implications.

GRAPHICAL ABSTRACT



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Keywords:
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Drinking water
UCMR3

ABSTRACT

This study examined data collected from U.S. public drinking water supplies in support of the recently-completed third round of the Unregulated Contaminant Monitoring Rule (UCMR3) to better understand the nature and occurrence of 1,4-dioxane and the basis for establishing drinking water standards. The purpose was to evaluate whether the occurrence data for this emerging but federally-unregulated contaminant fit with common conceptual models, including its persistence and the importance of groundwater contamination for potential exposure. 1,4-Dioxane was detected in samples from 21% of 4864 PWSs, and was in exceedance of the health-based reference concentration (0.35 μg/L) at 6.9% of these systems. In both measures, it ranked second among the 28 UCMR3 contaminants. Although much of the focus on 1,4-dioxane has been its role as a groundwater contaminant, the detection frequency for 1,4-dioxane in surface water was only marginally lower than in groundwater (by a factor of 1.25; $p < 0.0001$). However, groundwater concentrations were higher than those in surface water ($p < 0.0001$) and contributed to a higher frequency of exceeding the reference concentration (by a factor of 1.8, $p < 0.0001$), indicating that surface water sources tend to be more dilute. Sampling from large systems increased the likelihood that 1,4-dioxane was detected by a factor of 2.18 times relative to small systems ($p < 0.0001$). 1,4-Dioxane detections in drinking water were highly associated with detections of other chlorinated compounds particularly 1,1-dichlorethane (odds ratio = 47; $p < 0.0001$), which is associated with the release of 1,4-dioxane as a chlorinated solvent stabilizer. Based on aggregated nationwide data, 1,4-dioxane showed evidence of a decreasing trend in concentration and detection frequency over time. These data suggest that the loading to drinking

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Current Opinion in Environmental Science & Health

1,4-Dioxane in drinking water: emerging for 40 years and still unregulated

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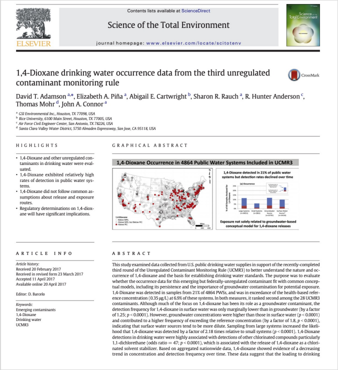
Stony Brook University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GRAPHICAL ABSTRACT

1,4-Dioxane Occurrence in 4864 Public Water Systems Included in UCMR3

1,4-Dioxane detected in 21% of public water systems but detection rates declined over time

Exposure not solely related to groundwater-based conceptual model for 1,4-dioxane releases

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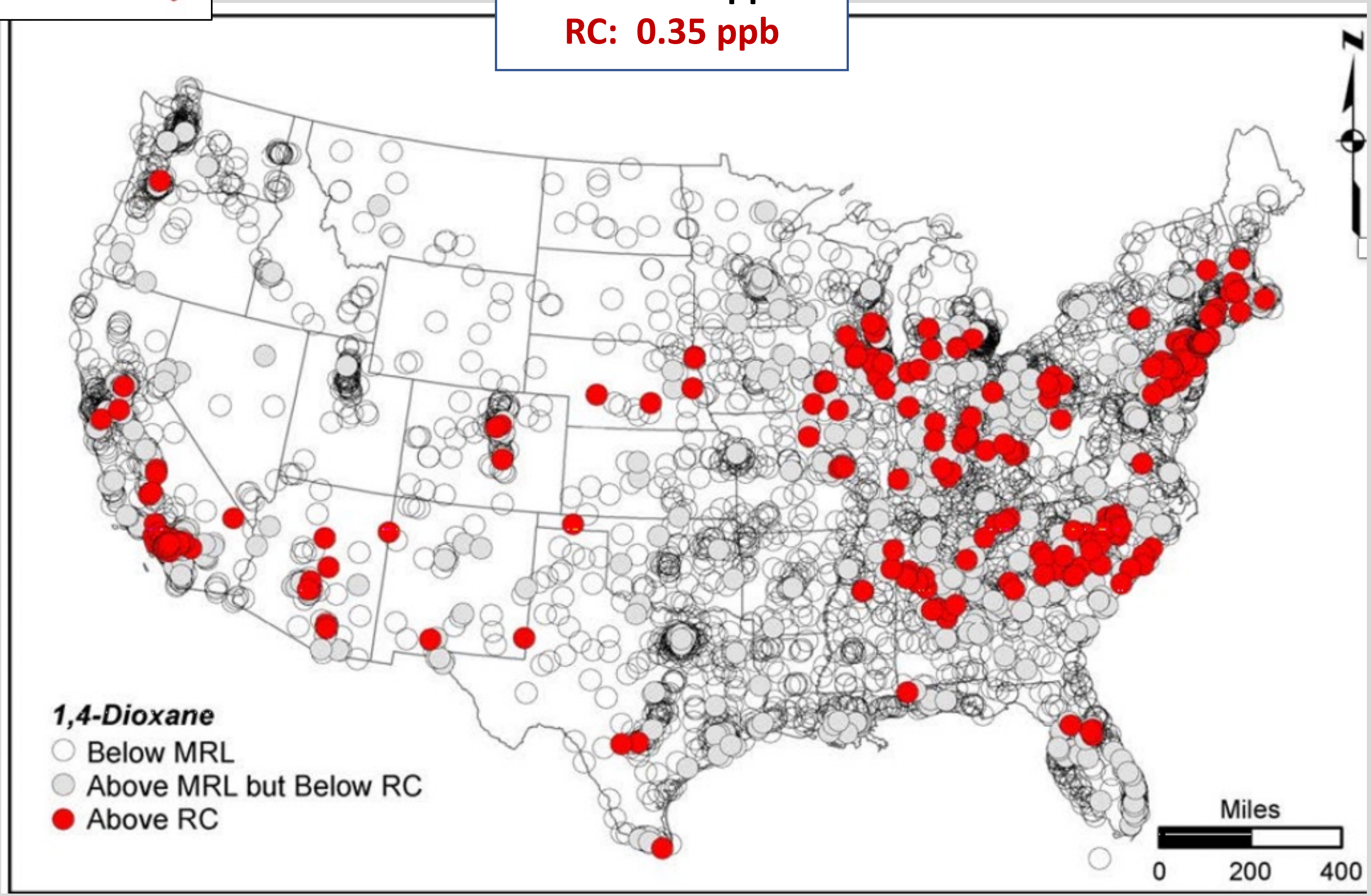
MRL: 0.07 ppb
RC: 0.35 ppb



1,4 Dioxane In water

Stony Brook University

Sources of 1,4-Dioxane

- Co-occur with chlorinated solvents at many contaminated sites
  - Particular 1,1,1-trichloroethane, due to its historic use as a stabilizer
- Used in paint strippers, dyes, greases, varnishes, and waxes
- Impurity in antifreeze and aircraft deicing fluids
- By-product in the manufacture of polyethylene terephthalate (PET) plastic
- Purifying agent in the manufacture of pharmaceuticals

Stony Brook University

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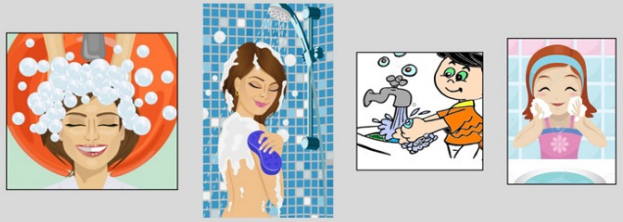
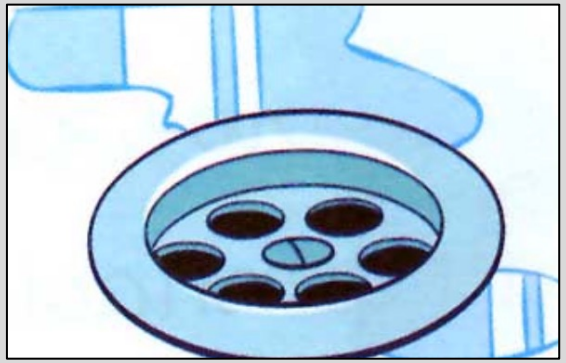
- Used in paint strippers, dyes, greases, varnishes, and waxes
- Impurity in antifreeze and aircraft deicing fluids
- Consumer products: deodorants, shampoos, and cosmetics
- By-product in the manufacture of polyethylene terephthalate (PET) plastic
- Purifying agent in the manufacture of pharmaceuticals



Rinse-off

1 ppm max

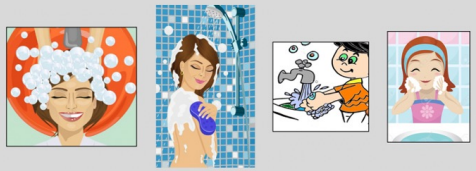
1, 4 D ends in drinking water



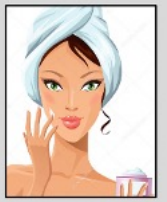
"Only the dose makes the poison"

Ingestion | Dermal | Inhalation

Paracelsus (1493-1541)



Rinse-off

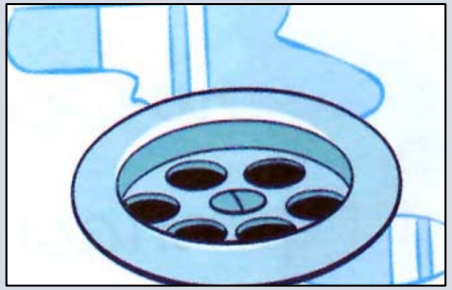


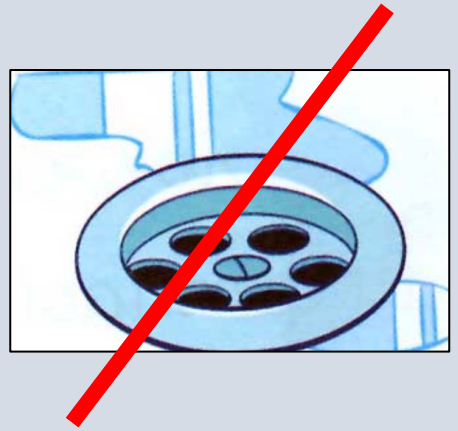
Leave-on

1 ppm

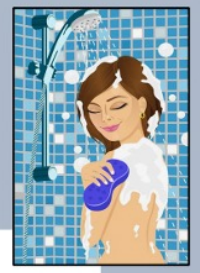
10 ppm

1,4 D ends in the water we drink





2- Develop technology to reduce 1,4 D



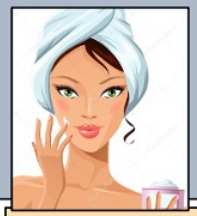
High 1,4 D

Sulfates
Sulfates
Ether Sulfates

Sulfonates
Olefin Sulfonates
Isethionates
Taurates
Sulfoacetates
Sulfosuccinates
Sulfolaurates

"Aminoacid" Type
Glycinates
Glutamates
Sarcosinates

Crypto Anionics
Carboxylates
Phosphates



Very low 1,4 D

ANIONICS
Carboxylates (M+)
Sulfates (M+)

CATIONICS
Di stearyl dimonium chloride

CRYPTO-ANIONICS
Alky (Ether) Phosphates (M+)
Alkyl Ether Citrates (M+)

NON-IONICS
Glyceryl Esters →
Sorbitan Esters →
Glucosides Esters →
Sucrose Esters
Polyglyceryl Esters

Ethoxylated F. Alcohols
Ethoxylated Fatty Acids
Ethoxylated Glyceryl Esters
Ethoxylated Sorbitan Esters
Ethoxylated Glucoside Esters

2- Develop technology to reduce 1,4 D

Very low 1,4 D

ANIONICS

Carboxylates (M+)

Sulfates (M+)

CATIONICS

Di stearyl dimonium chloride

CRYPTO-ANIONICS

Alky (Ether) Phosphates (M+)

Alkyl Ether Citrates (M+)

Ethoxylated F. Alcohols

Ethoxylated Fatty Acids

Ethoxylated Glyceryl Esters

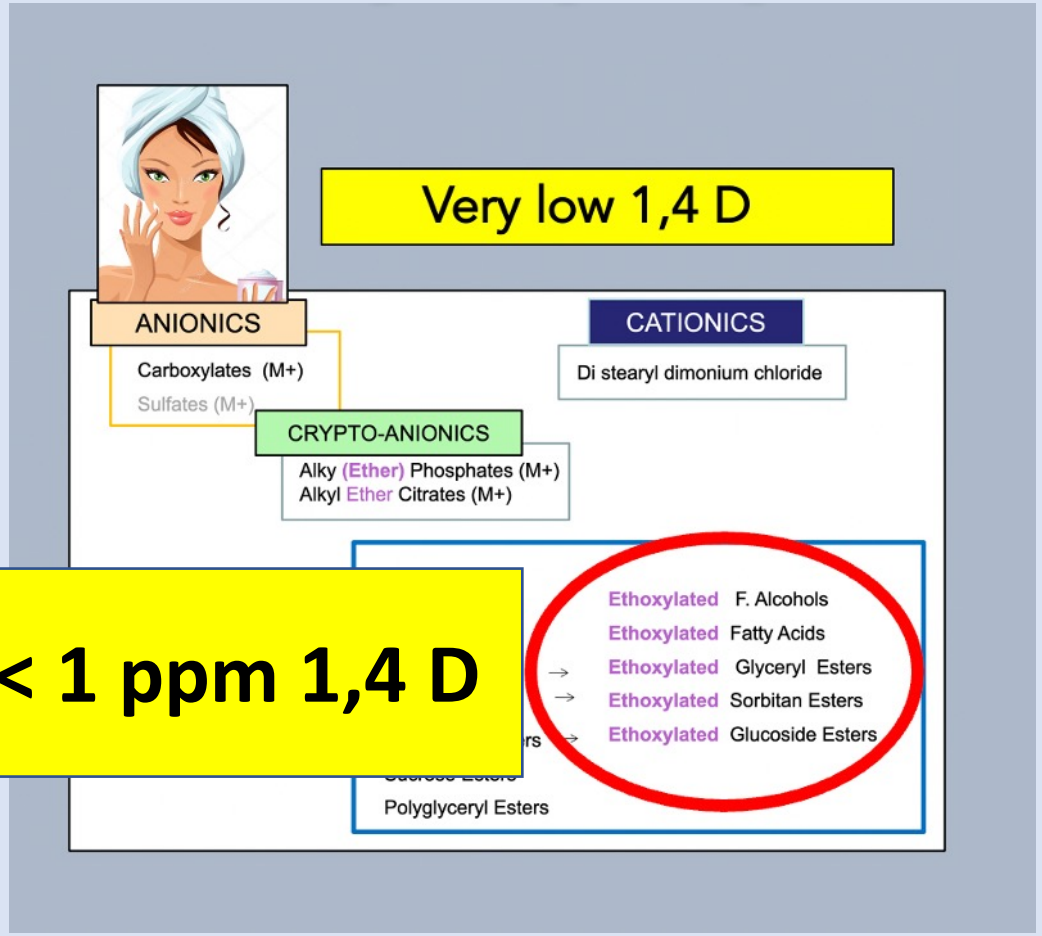
Ethoxylated Sorbitan Esters

Ethoxylated Glucoside Esters

Polyglyceryl Esters

< 1 ppm 1,4 D

Assume a cream with 3 % ethoxylated emulsifier



How much 1,4 Dioxane will be on the skin per 1 gram of emulsion ?

- 0.03 g
- 0.003 g
- 0.0003 g
- 0.00003 g
- 0.000003 g
- 0.0000003 g

How much 1,4 Dioxane will be on the skin per 1 gram of emulsion ?

0.03 g

0.003 g

0.0003 g

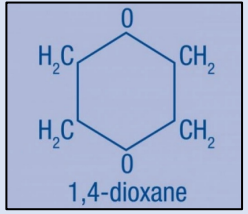
0.00003 g

0.000003 g

0.0000003 g

End 2022: **10 ppm.**

NO IMPACT



Of this amount, how much will evaporate ?

0.03 g

0.003 g

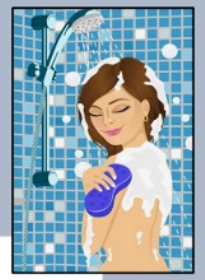
0.0003 g

0.00003 g

0.000003 g

0.0000003 g

2- Develop technology to reduce 1,4 D



High 1,4 D

Sulfates
Sulfates
Ether Sulfates

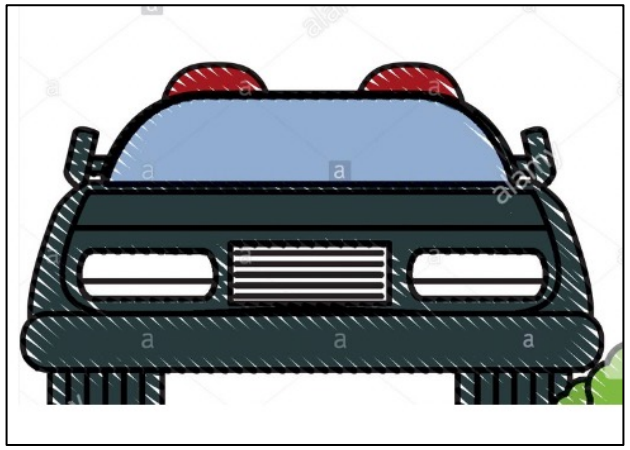
Sulfonates
Olefin Sulfonates
Isethionates
Taurates
Sulfoacetates
Sulfosuccinates
Sulfolaurates

"Aminoacid" Type
Glycinates
Glutamates
Sarcosinates

Crypto Anionics
Carboxylates
Phosphates

Rinse-off

- **End 2023: 1 ppm**



How much ?

SLES at 70 % high 1,4 D
$ 1.6 / kg

SLES at 70 % low 1,4 D
$ 2.5 / kg

1.5 times more expensive

SLES at 70 % high 1,4 D
$ 1.6 / kg

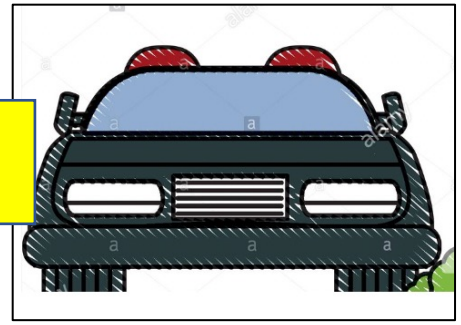
SLES at 70 % low 1,4 D
$ 2.5 / kg

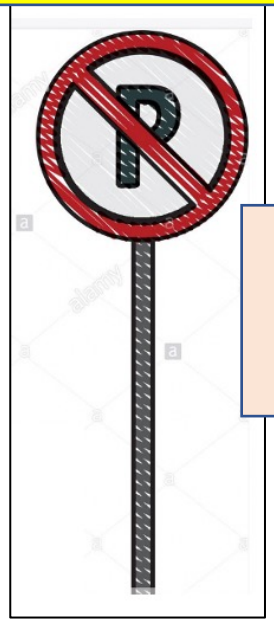
1.5 times more expensive

Cocoyl Methyl Isethionate at 70 %
$ 9.1 /kg

3.5 times more expensive

“Free”





Very Bad Call

REAL COSMETIC INDUSTRY

Chemical Industry

COSMETICS

"The marketing concept of 'clean' beauty challenges the safety and efficacy of products not deemed 'clean' by indirectly labeling them as 'dirty'.

It disregards the important work of scientists around the world making a monumental effort to evaluate a complete body of evidence to formulate the products that you know and love"

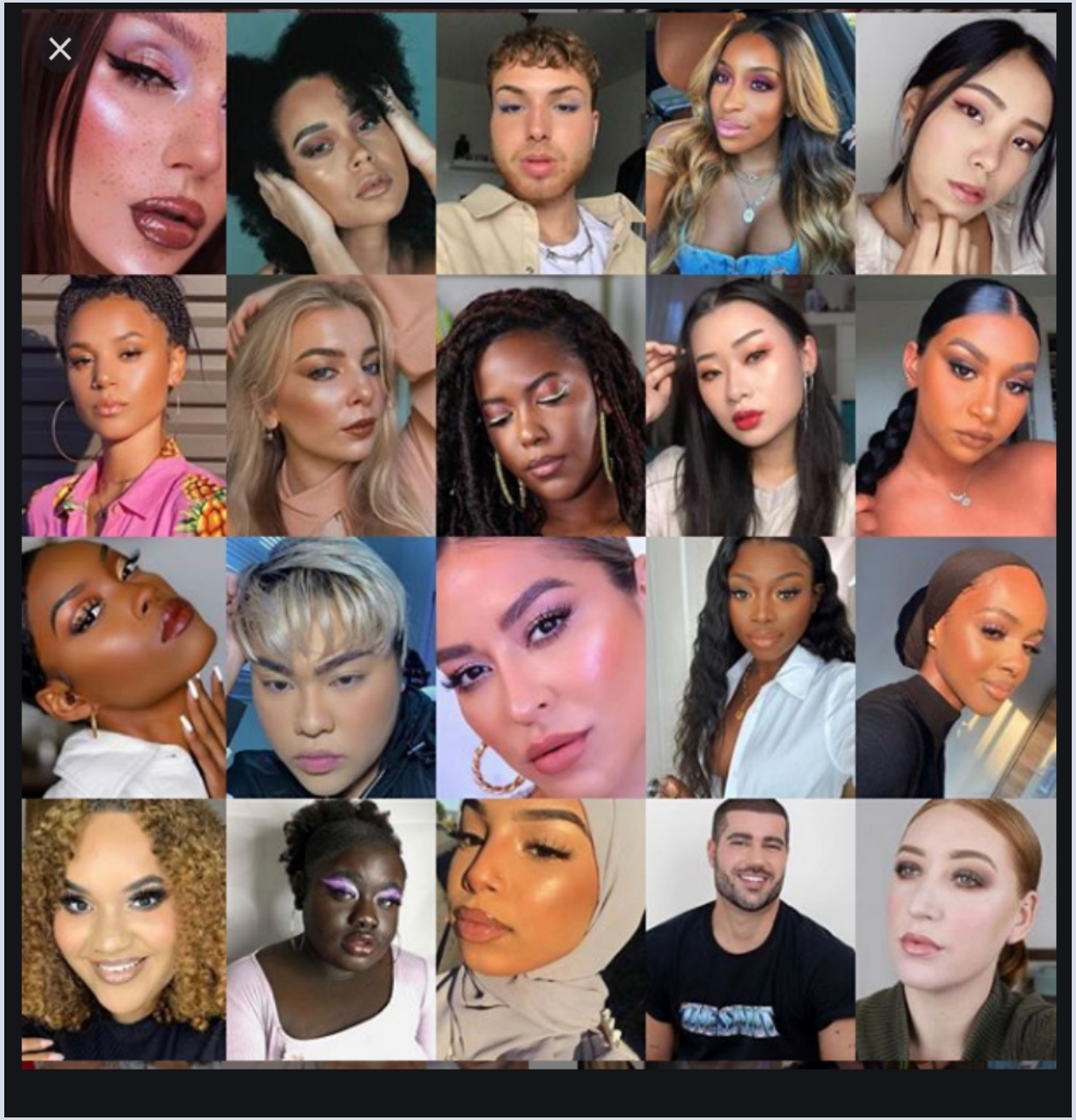
Response of MEDIOCRITY

1995 “Natural”

2005 ”Sulfate-Free”

2010 “Clean Beauty”

Industry of “P”



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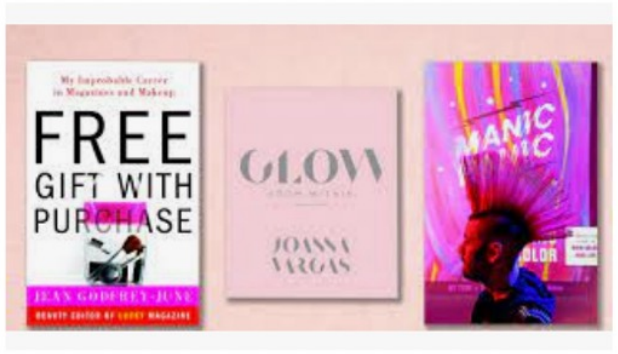

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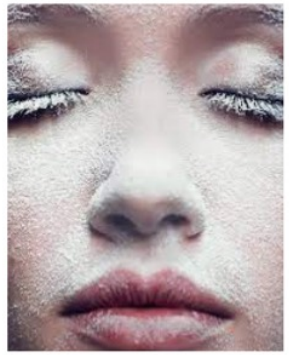

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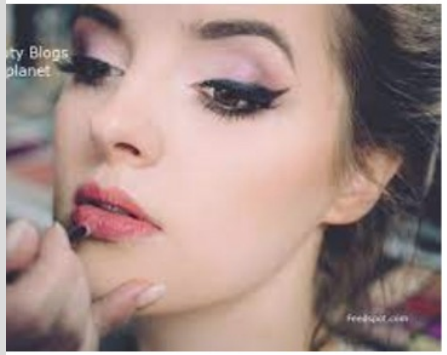

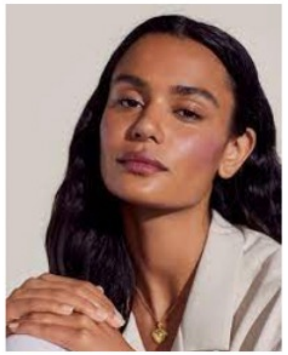

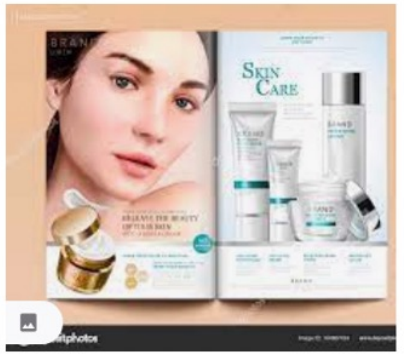

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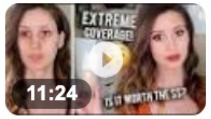

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