Paint and Varnish Strippers: Availability of Safer Alternatives & Requirements for Meeting Stage 1 of the California Safer Consumer Products Regulations

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A Project of:

BizNGO
FOR SAFER CHEMICALS AND SUSTAINABLE MATERIALS

Alternatives Assessment Working Group

Outline for today

- Context setting, project goals & results for first steps of the CA SCP process (Molly Jacobs)
- GreenScreen® for Safer Chemicals Assessment of Alternatives (Bingxuan Wang)
- Lessons learned from this demonstration project (Molly Jacobs)
- Q&A (Mark Rossi)

Context: Stage 1 Assessment

- The California SCP regulations divide alternatives analysis into two stages.
- Stage 1 includes:
  - Identifying the product's and chemical of concern's function and performance requirements
  - Identifying candidate alternatives
  - Identifying relevant comparison factors (for example, environmental, human health, and physicochemical properties)
  - Assessing hazards associated with the relevant factors identified
  - Assessing additional information
  - Developing a work plan and associated timeline relevant to completion and submission of the final report (outlining timeline & steps for the Stage 2 assessment)
- NOT included in Stage 1 (included in Stage 2)
  - Performance & economic feasibility assessments
  - Life cycle impacts

Demonstration Project Goals

1. Identify less hazardous alternatives to methylene chloride in formulated paint stripper products

2. Identify candidate alternatives for methylene chloride in paint stripping formulations that will likely be considered in actual/future Stage 1 submissions for this "priority product" in CA

3. Identify challenges and needs confronting compliance with the alternatives analysis process under the CA SCP regulations

Note: Project followed the CA SCP regulations – DTSC's draft guidance not published at the time of this project

Perspective: Chemical Product Formulator

- The regulations requires compliance by "responsible entities" associated with a priority product:
  - Manufacturers
  - Importers
  - Assemblers
  - Retailers

Photo by Jamie Smith Hopkins/Center for Public Integrity

- Project conducted from the perspective of a chemical products formulator (not tied to any real company or product)

Functional Requirements: Product & Chemical of Concern

- Paint strippers function: paint removal
- Methylene chloride (chemical of concern) in paint stripper is the stripping ***solvent***
  - the solvent penetrates the paint layers and breaks the bond between the paint and the substrate
  - as $MeCl_2$ volatizes, it pushes up on the resulting paint film, tenting it away from the substrate
  - paint can be subsequently remove with a blunt surface such as a puddy knife
- **Functional use = Solvent**
  - Key to the decision logic used about what alternatives to consider

Photo by: House-Painting info.com

Performance Requirements

Performance Standards for chemical paint removers

- ASTM D6189
- GreenSeal GS52

Primary Metrics

- % of coatings removed in a specific time period (e.g., 30 minutes/1hr)
- Condition of surface substrate once paint removed

Performance factors

- Time to strip
- Compatibility with substrate
- Effectiveness in removing a variety of coatings

Methylene Chloride Paint Strippers A formulated product

- Methylene chloride in paint strippers work in conjunction with other chemicals
  - Co-solvents (e.g. methanol and/or acetone)
  - Including activators (phenol)
  - Evaporation inhibitors
  - Thickeners
  - Wetting agents
  - Emulsifiers
  - Corrosion inhibitors
- Important to ensure changes in product formulation are indeed SAFER

Identification of Alternatives

Physical/mechanical stripping – use of abrasion techniques

- Scraping, sanding, media blasting (e.g., plastic media blasting, wheat media blasting, liquid nitrogen blasting, etc.)

Pyrolytic/thermal stripping – use of thermodynamic methods

- Heat guns, laser stripping

Chemical stripping

- Alkaline strippers (including caustic strippers), acid strippers and solvent strippers

Alternatives considered

1. **Considered:** only consumer/professional uses
   - **Industrial alternatives not considered**
     - Media blasting, some laser/thermal techniques that require use in off-site facilities, systems that require industrial immersion techniques
2. **Considered** alternatives that can replace $MeCl_2$ solvent function in the paint stripper & other alternatives that are w/in the business model of a chemical products formulator to consider
   - **Physical/mechanical techniques not considered**

Sources Used to Identify Alternatives

- **Identified alternatives based on a literature review of *publicly available* documents.** Examples:
  - Policy Analysts Limited. *Impact Assessment of Potential Restrictions on the Marketing and of Dichloromethane in Paint Strippers.* Prepared for the European Commission Directorate-General Enterprise and Industry. 2007.
  - Morris M and Wolf K. Methylene Chloride Consumer Product Paint Strippers: Low-VOC, Low Toxicity Alternatives. May 2006.
  - Washington State Dept. of Labor & Industries, SHARP. Successful Bathtub Stripping with Benzyl Alcohol as an Alternative to Methylene Chloride. 2012.
- ***Identified 11 priority alternatives.*** *Primary criteria:*
  - *Being used in existing paint strippers on the market based on* a review of existing MSDS
  - Case study experience
  - Those also likely considered by DTSC as referenced in its *Priority Product Profile* report
  - Identified, but did not not include n-Methylpyrrolidone (nMP) – DTSC stated it should not be considered as it's on CA Prop 65 list (reproductive toxicant)
- The 11 alternatives ***should not* be considered comprehensive**

Relevant Comparison Factors

Considered relevant if: *"...the factor makes a material contribution to one or more adverse public health impacts, adverse environmental impacts, adverse waste and end-of-life effects, or materials and resource consumption; and there is a material difference in the factor's contribution to impacts between the Priority Product and alternative(s) under consideration"*

1. Adverse environmental impacts [stage 1 & 2]
2. Adverse public health impacts [Stage 1]
3. Adverse waste and end-of-life impacts [Stage 1]
4. Environmental fate [Stage 1 & 2]
5. Materials and resource consumption impacts [Stage 2]
6. Physical chemical hazards [Stage 1]
7. Physiochemical properties [Stage 1 & 2]
8. Associated exposure pathways and life cycle segments [Stage 1 & 2]

Hazard Assessment

Using GreenScreen® for Safer Chemicals Methodology

GreenScreen® for Safer Chemicals

- A hazard assessment tool developed by Clean Production Action
- Useful for comparative Chemical Hazard Assessment (CHA)
- Built on
  - National and international authoritative lists of chemicals of concern
  - U.S. EPA's Design for the Environment (DfE) Alternatives Assessment Criteria
  - Globally Harmonized System of Classification and Labeling of Chemicals (GHS)
- The method is freely and publically accessible, transparent and peer reviewed
- Most current method version: v 1.2

All supporting resources at: http://www.cleanproduction.org/Greenscreen.v1-2.php

GreenScreen® for Safer Chemicals

- Evaluates 18 hazards endpoints

Human Health Group I	Human Health Group II and II*	Environmental Toxicity & Fate	Physical Hazards
Carcinogenicity	Acute Toxicity	Acute Aquatic Toxicity	Reactivity
Mutagenicity & Genotoxicity	Systemic Toxicity & Organ Effects	Chronic Aquatic Toxicity	Flammability
Reproductive Toxicity	Neurotoxicity	Other Ecotoxicity studies when available	
Developmental Toxicity	Skin Sensitization	Persistence	
Endocrine Activity	Respiratory Sensitization	Bioaccumulation	
	Skin Irritation		
	Eye Irritation		

GreenScreen® for Safer Chemicals

A decision framework that weights hazard endpoints and classifications to establish Benchmark scores (CMR and PBT carry more weight)

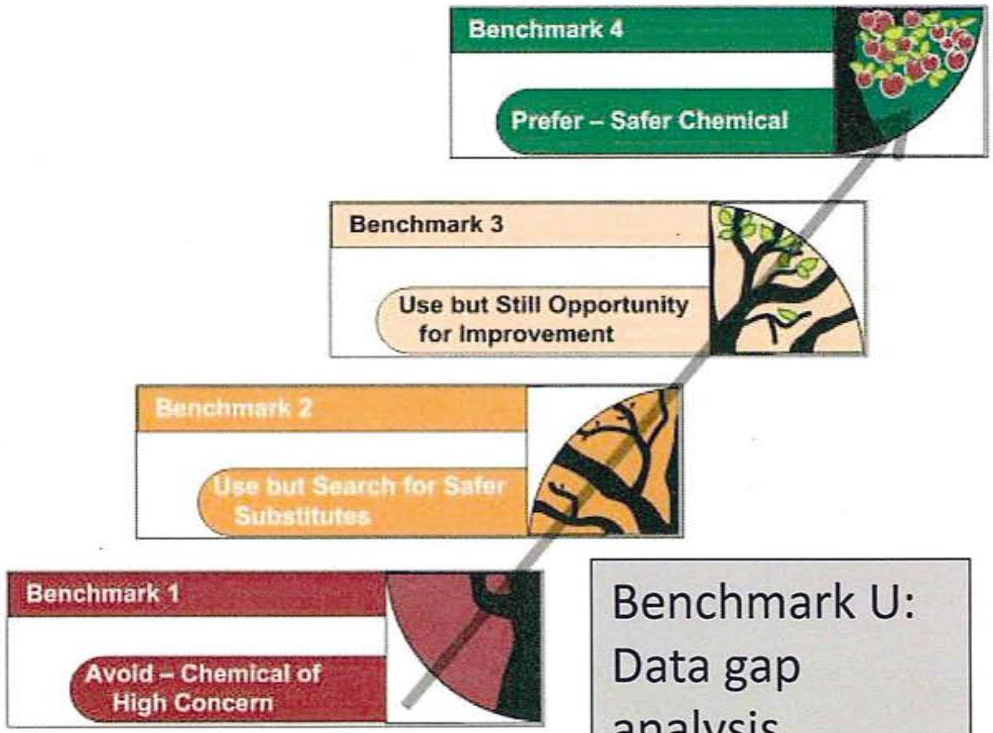
BM1 – Avoid/Phase out

BM2 – Use but search for safer substitutes

BM3 – Use but still opportunity for improvement

BM4 – Inherently how hazard

BMU – Unspecified due to insufficient data



GreenScreen® for Safer Chemicals

- Different levels of effort
  - GreenScreen® List Translator
    - Automated tool that screens the chemicals against all GS-specified authoritative and screening lists
    - Scores: LT-1 (equivalent to BM 1), LT-P1, LT-U
  - Full GreenScreen®
- 12 GreenScreen®s in this report
  - 10 performed by ToxServices, LLC
  - 2 conducted by Dr. Brian Pentilla (methylene chloride and toluene, publically available from Interstate Chemicals Clearinghouse (IC2))

TOXSERVICES
TOXICOLOGY RISK ASSESSMENT CONSULTING

IC2 INTERSTATE CHEMICALS CLEARINGHOUSE

GREENSCREEN® FOR SAFER CHEMICALS

GreenScreen® Evaluation of Methylene Chloride and Its Alternatives - Overview

Chemical	CASRN	Benchmark Score
Methylene chloride	75-09-2	1
Benzyl alcohol	100-51-6	2
2-(2-butoxyethoxy) ethanol	112-34-5	2
Dimethyl sulfoxide (DMSO)	67-68-5	3
1,3-dioxolane	646-06-0	2
Estasol (dibasic esters mixture)l	95481-62-2	2
d-Limonene	5989-27-5	2
Acetone	67-64-1	2
Methanol	67-56-1	1
Toluene	108-88-3	1
Formic acid	64-18-6	2
Caustic soda	1310-73-2	2

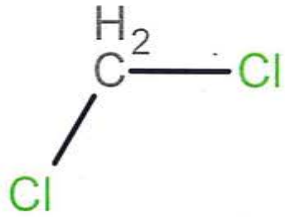
GreenScreen® Evaluation of Methylene Chloride and Its Alternatives - Overview

		Group I Human					Group II & II Human									Ecotox		Fate		Physical	
Chemical Name	CASRN	C	M	R	D	E	AT	ST		N		SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F
								Single	repeated	Single	repeated										
Methylene chloride	75-09-2	H	NE	DG	DG	M	M	vH	H	vH	vH	L	DG	H	H	M	L	vH	vL	L	L
Benzyl alcohol	100-51-6	L	L	L	M	DG	M	L	L	M	H	H	L	L	H	L	L	vL	vL	L	L
2-(2-butoxyethooxy) ethanol	112-34-5	L	L	L	L	DG	L	L	H	DG	L	L	DG	M	H	L	L	vL	vL	L	M
Dimethyl sulfoxide	67-68-5	L	L	L	L	DG	L	L	L	L	L	L	L	M	M	L	L	L	vL	L	M
1,3-dioxolane	646-06-0	L	M	M	M	DG	L	M	M	M	L	L	DG	M	H	L	L	M	vL	L	H
Estasol (dibasic esters mixture)	95481-62-2	L	L	L	M	M	L	M	M	M	DG	L	DG	L	M	M	L	vL	vL	M	L
d-Limonene	5989-27-5	L	L	DG	L	DG	L	L	L	DG	DG	H	DG	H	H	vH	H	vL	M	L	M
Acetone	67-64-1	L	L	M	M	DG	L	M	M	M	M	L	DG	L	H	L	L	vL	vL	L	H
Methanol	67-56-1	NA	NA	NA	H	NA	H	vH	NA	NA	NA	NA	NA	NA	NA	L	L	vL	vL	NA	H
Toluene	108-88-3	DG	L	H	H	M	L	M	H	M	H	L	DG	H	L	H	H	H	vL	L	H
Formic acid	64-18-6	L	L	L	L	DG	H	vH	H	vH	DG	L	DG	vH	vH	M	M	vL	vL	L	M
Caustic soda	1310-73-2	L	L	L	L	L	H	vH	L	L	L	L	DG	vH	vH	M	DG	L	vL	M	L

GreenScreen Benchmark™ 1 Chemicals

		Group I Human					Group II & II Human									Ecotox		Fate		Physical	
Chemical	CASRN	C	M	R	D	E	AT	ST		N		SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F
								Single	repeated	Single	repeated										
Methylene chloride	75-09-2	H	NA	DG	DG	M	*M*	*vH*	H	*vH*	*H*	L	DG	H	H	M	*L*	*vH*	vL	L	L

- Methylene chloride (CMR and vPvT)
  - Uses: solvent, propellant in aerosol products, postharvest fumigant for grains and strawberries and degreening agent for citrus fruit
  - Critical hazards:
    - Cancer (+ persistence (air))
    - Neurotoxicity + persistence
    - Systemic toxicity (fatty change in the liver) + persistence



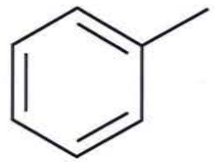
GreenScreen Benchmark™ 1 Chemicals

		Group I Human					Group II & II Human									Ecotox		Fate		Physical	
Chemical	CASRN	C	M	R	D	E	AT	ST		N		SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F
								Single	repeated	Single	repeated										
Methanol	67-56-1	NA	NA	NA	H	NA	H	vH	NA	NA	NA	NA	NA	NA	NA	L	*L*	vL	*vL*	NA	H
Toluene	108-88-3	DG	L	H	H	M	L	M	H	M	H	L	DG	H	L	H	*H*	*H*	vL	L	H

- Methanol (CMR)

  - Solvent, antifreeze, octane booster in gasoline
  - Abbreviated screen based primarily on authoritative listings (List Translator tool)
  - Critical hazards: developmental toxicity (teratogen)

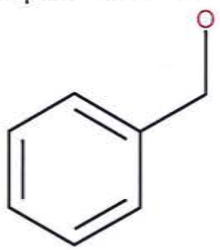
- Toluene (CMR)
  - Octane booster in gasoline, production of benzene and polymers
  - Critical hazards: developmental toxicity (developmental neurotoxicant), reproductive toxicity



GreenScreen Benchmark™ 2 Chemicals

		Group I Human					Group II & II Human									Ecotox		Fate		Physical	
Chemical	CASRN	C	M	R	D	E	AT	ST		N		SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F
								Single	repeated	Single	repeated										
Benzyl alcohol	100-51-6	L	L	*L*	*M*	DG	M	L	L	*M*	*H*	H	*L*	L	H	L	L	vL	vL	*L*	L
2-(2-Butoxyethooxy) ethanol	112-34-5	*L*	L	L	L	DG	L	L	H	DG	L	L	DG	*M*	H	L	L	vL	vL	*L*	M

- Benzyl alcohol
  - Solvent, plasticizer, fragrance, flavoring, preservative, viscosity-control, degreasing agent
  - Critical hazards: developmental toxicity, neurotoxicity (repeated dose), skin sensitization

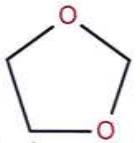


- 2-(2-Butoxyethoxy)ethanol
  - Solvent, intermediate for chemical synthesis
  - Critical hazards: systemic toxicity (repeated dose)

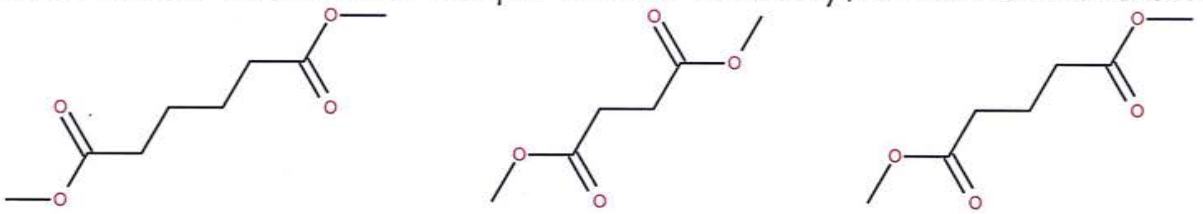
GreenScreen Benchmark™ 2 Chemicals

		Group I Human					Group II & II Human									Ecotox		Fate		Physical	
Chemical	CASRN	C	M	R	D	E	AT	ST		N		SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F
								Single	repeated	Single	repeated										
1,3-dioxolane	646-06-0	L	*M*	*M*	M	DG	L	M	M	M	L	L	DG	*M*	*H*	L	L	*M*	vL	*L*	H
Estasol (dibasic esters mixture)	95481-62-2	*L*	L	*L*	*M*	*M*	L	M	*M*	M	DG	L	DG	L	*M*	M	*L*	vL	vL	*M*	L

- 1,3-Dioxolane
  - Monomer for polyacetals, chemical intermediate, process solvent, stabilizer for halogenated solvents
  - Critical hazards: mutagenicity, reproductive toxicity, developmental toxicity, flammability



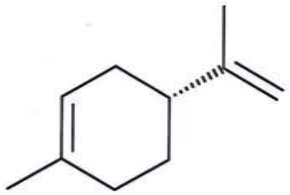
- Estasol (Dibasic dimethyl esters of adipic acid, succinic acid & glutaric acid)
  - Solvent, plasticizer, polymer intermediate
  - Critical hazards: developmental toxicity, endocrine activity



GreenScreen Benchmark™ 2 Chemicals

Chemical	CASRN	Group I Human					Group II & II Human									Ecotox		Fate		Physical	
		C	M	R	D	E	AT	ST		N		SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F
								Single	repeated	Single	repeated										
d-Limonene	5989-27-5	L	L	DG	L	DG	L	L	L	DG	DG	H	DG	H	*H*	vH	H	vL	M	*L*	M
Acetone	67-64-1	*L*	L	*M*	M	DG	L	*M*	M	M	*M*	L	DG	L	H	L	L	vL	vL	L	H

- D-Limonene
  - Solvent, fragrance ingredient, flavoring agent
  - Critical hazards: skin sensitization, acute aquatic toxicity

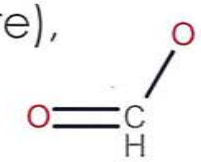


- Acetone
  - Chemical feedstock, solvent
  - Critical hazards: reproductive toxicity, developmental toxicity, flammability

GreenScreen Benchmark™ 2 Chemicals

		Group I Human					Group II & II Human									Ecotox		Fate		Physical	
Chemical	CASRN	C	M	R	D	E	AT	ST		N		SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F
								Single	repeated	Single	repeated										
Formic acid	64-18-6	L	L	L	*L*	DG	H	vH	*H*	vH	DG	L	DG	vH	vH	M	M	vL	vL	L	M
Caustic soda	1310-73-2	*L*	L	*L*	*L*	*L*	H	vH	*L*	*L*	*L*	L	DG	vH	vH	M	DG	*L*	*vL*	*M*	L

- Formic acid
  - Textile dyeing, rubber manufacture, chemical intermediate, catalyst in resins, preservative, acidifying agent, food additive, corrosion inhibitor
  - Critical hazards: systemic toxicity (single and repeated exposure), neurotoxicity (single dose), skin and eye irritation

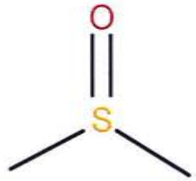


- Caustic soda
  - pH regulation, alkaline ore digestion, chemical intermediate, saponification of fats and oils, degreaser and cleaner in food industry
  - Critical hazards: systemic toxicity (single dose), skin and eye irritation

GreenScreen Benchmark™ 3 Chemical

		Group I Human					Group II & II Human									Ecotox		Fate		Physical	
Chemical	CASRN	C	M	R	D	E	AT	ST		N		SnS	SnR	IrS	IrE	AA	CA	P	B	RX	F
								Single	repeated	Single	repeated										
Dimethyl sulfoxide	67-68-5	*L*	L	L	L	DG	L	L	L	L	L	L	L	*M*	*M*	L	*L*	*L*	vL	*L*	M

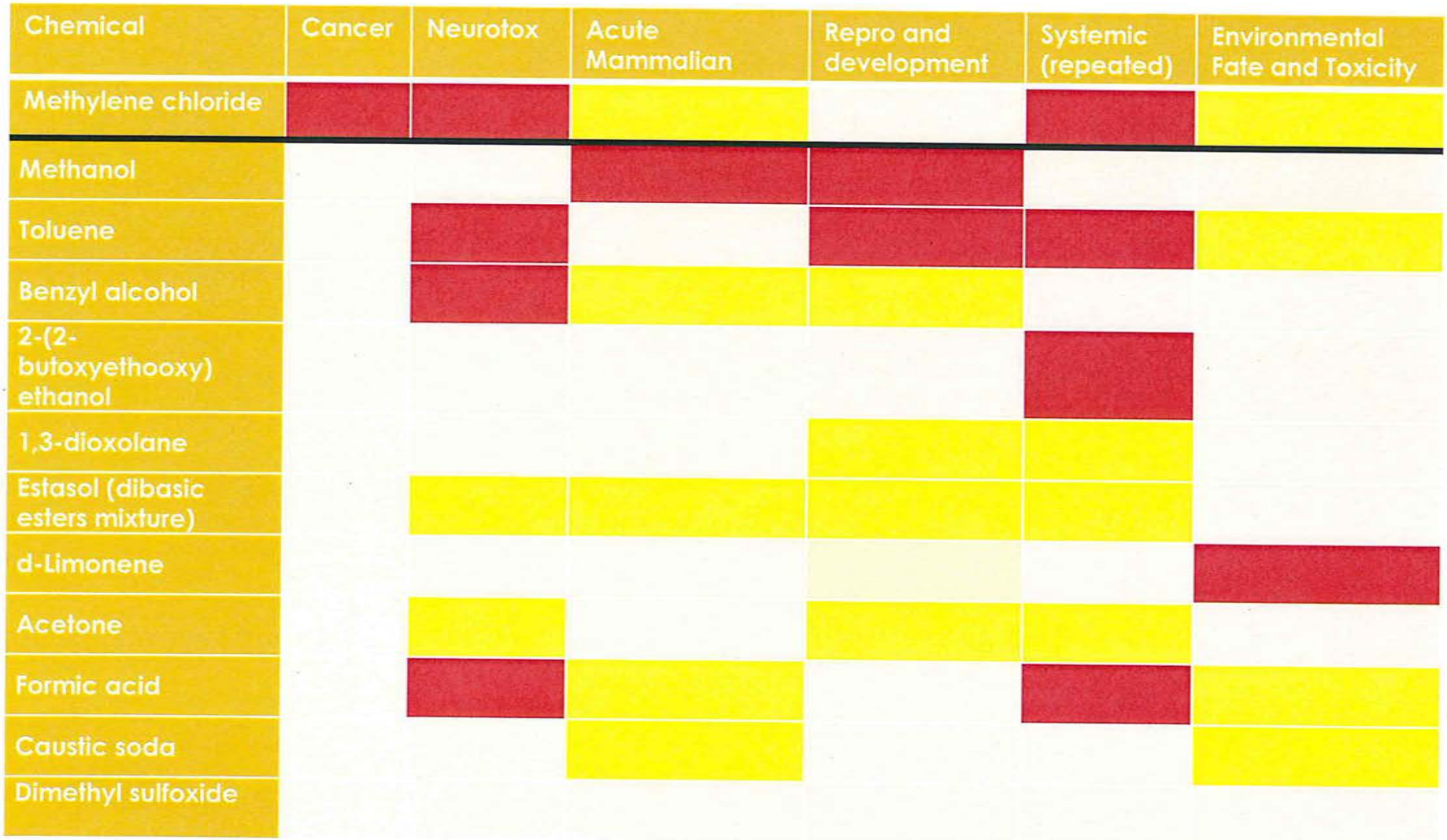
- Dimethyl sulfoxide (DMSO)
  - Solvent, analytical reagent, chemical intermediate, preservative, treatment of interstitial cystitis
  - Critical hazards: skin and eye irritation, flammability
  - However, DMSO is a penetration enhancer, increasing the absorption (and toxicity) of other ingredients in the formulation.
  - Should DMSO be further considered as a potential alternative given Stage 2 analysis results, a deeper examination of the hazards of other formulation chemicals is *essential*



Further Analysis of GS Benchmark™ 2 and 3 Chemicals

Chemical	Moderate Group I Human	Very High Group II Human	High Group II* Human	Very High Ecotoxicity	Flammability
Benzyl alcohol	X		X		
2-(2-Butoxyethoxy) ethanol			X		
1,3-Dioxolane	X				X
Estasol (dibasic esters mixture)	X				
d-Limonene			X	X	
Acetone	X				X
Formic acid		X	X		
Caustic soda		X			
DMSO					

Common Toxicological Concerns for Solvents



U.S. EPA Safer Chemical Ingredients List (SCIL)

Chemical	Benchmark Score	SCIL Status	Notes
2-(2-Butoxyethoxy) ethanol	2	Yellow Triangle	Hazardous Air Pollutant under the Clean Air Act and a volatile organic compound (VOC)
d-Limonene	2	Yellow Triangle	The potential to accelerate formation of oxidation products (can't be used in combination with oxidizers such as H_2O_2) Aquatic toxicity
Formic acid	2	Full Green Circle	
Caustic soda	2	Full Green Circle	

- Some of the GreenScreen® Benchmark 2 chemicals are listed by the U.S. EPA Safer Choice Program as "safer ingredients"
  - SCIL Yellow Triangle: The chemical has met Safer Choice Criteria for its functional ingredient-class, but has some hazard profile issues. It is a best-in-class chemical and among the safest available for a particular function.
  - SCIL Full Green Circle: The chemical has been verified to be of low concern based on experimental and modeled data.

Chemicals De-Selected for Stage 2

Chemical	CASRN	Benchmark Score
Methylene chloride	75-09-2	1
Benzyl alcohol	100-51-6	2
2-(2-butoxyethooxy) ethanol	112-34-5	2
Dimethyl sulfoxide (DMSO)	67-68-5	3
1,3-dioxolane	646-06-0	2
Estasol (dibasic esters mixture)l	95481-62-2	2
d-Limonene	5989-27-5	2
Acetone	67-64-1	2
Methanol	67-56-1	1
Toluene	108-88-3	1
Formic acid	64-18-6	2
Caustic soda	1310-73-2	2

Summary of Hazard Assessment Results

- Two alternatives (methanol and toluene) were screened out due to high developmental/reproductive toxicity (BM 1)
- The remaining alternatives were safer, yet not free of hazards
- DMSO has the lowest hazard profile (BM 3), but it can potentiate the hazards of other substances
- GreenScreen® is a useful tool in hazard assessment in AA, and it applies greater weight on CMR (Group I Human Health) and PBT endpoints compared to Group II/II* Human Health or Ecotoxicity
- Additional information about a substance – such as conditions of use – needs to be considered as well

Lessons Learned

Lesson Learned #1: Information is readily available

Information was **readily & publicly** available to address the CA SCP requirements of a Stage 1 Analysis

- Information on:
  - Functional requirements
  - Performance requirements
  - Potential alternatives

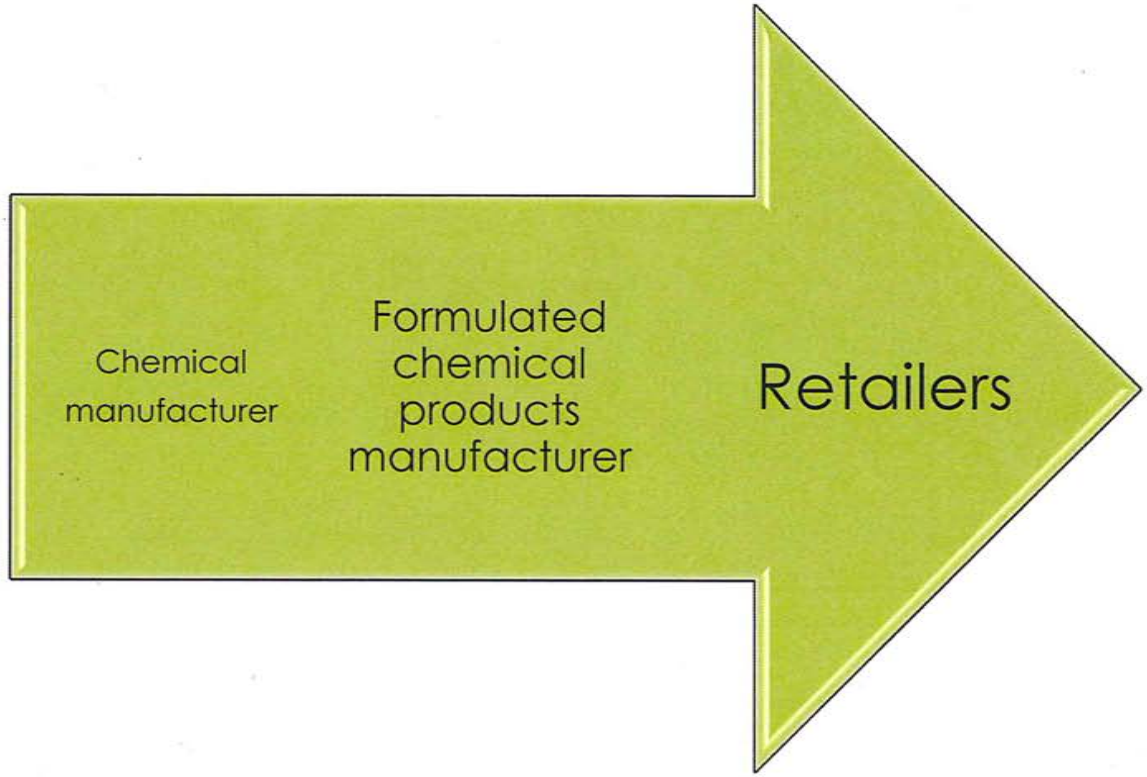
Lesson 2: Safer alternatives are available

Based on GreenScreen® assessments of the 11 alternatives, safer alternatives to methylene chloride for use in chemical paint strippers are available

- **What is a sufficient # of alternatives to evaluate?**
  - There's no magic number
  - Hazard assessments are resource intensive
  - Technical & economic feasibility addressed in Stage 2 – need to ensure that feasibility is considered to some degree when screening alternatives

Lesson 3: Alternatives considered should be informed by the firm's ability to adopt those alternatives

- Action-orientation of alternatives analysis should guide the process from the start
- Type and range of alternatives to consider should be informed by the capacity of business entities to adopt those alternatives



Lesson 3 is NOT ideal, but realistic

- CA SCP regulations designed to minimize regrettable substitutions
- Will compliance with the regulation showcase the full range of alternatives?
  - Essential for research institutions, public health & environmental organizations to be prepared to provide additional information to support DTSC during public comment periods.

Lesson 4: GreenScreen® useful for evaluating hazards, but sufficient?

- Project **demonstrated the utility** of using GreenScreen® for the hazard assessment step
- BizNGO had access to experts, **yet confronted questions of the sufficiency of our hazard assessments to meet the SCP regulations**
- Hazard assessments are an intensive process that requires technical expertise that only the largest of corporations typically have in-house
  - If GreenScreen assessments prove to be insufficient to meet the requirements of the SCP regulations, the costs to companies could be significant

Lesson 5: Hazards of other chemicals in formulation need to be assessed

It is unlikely that the alternatives assessed in this demonstration project can replace methylene chloride without reformulating the product to meet performance needs

- Additional assessment of hazards (or at minimum, a screen against authoritative hazard lists) should be performed for chemicals above a threshold percent concentration in the formulation (e.g., Safer Choice Program's = 0.01%)

Additional Recommendations

- For methylene chloride replacements in paint strippers:
  - Consider a broader range of chemical alternatives that require performance testing
    - New bio-based solvents: methyl soyate or ethyl lactate
    - Use tools such as the Hansen Solubility Parameters http://hansen-solubility.com/index.html
- Data permitting: consider a broader range of eco-toxicity endpoints
  - Additional eco-toxicity endpoints such as effects on organisms necessary for waste water treatment or terrestrial toxicity may be relevant for specific use scenarios of paint strippers
- Important to consider the hazards of all chemicals in a formulated chemical product: the goal of an alternatives assessment is to ensure the final product is safer overall

Concluding Remarks

Alternatives analysis as being advanced by the California SCP regulation is one of the most important developments in recent years to advance the supply of safer chemicals and products

CA SCP regulation provides a framework & the opportunity for firms to identify that safer alternatives are available and are viable from a business perspective

Fulfilling the opportunities require working through some of the needs & challenges identified in this demonstration project

Questions?

- Slides & presentation available at www.bizngo.org
- Questions: bizngo@cleanproduction.org

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