Alternatives to Methylisothiazolinone and Chloromethylisothiazolinone in Leather Tanning

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Leather Tanning Process

- **LOTS of chemicals are used in leather production**
- Chromates (80-95% of production), vegetable tannins or glutaraldehyde
- Fatliquoring agents
- Dyes, pigments and related chemicals
- Adhesives
- Finishes
- Antimicrobials

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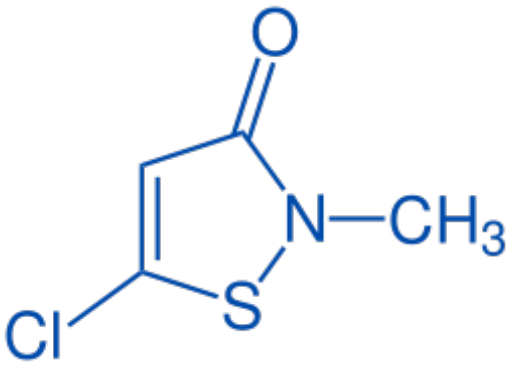
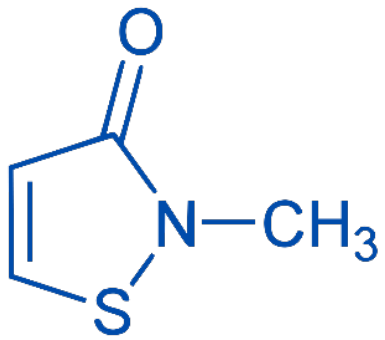
Leather Preservatives and Skin Sensitization

- Isothiazolones
  - Widely used in leather and other consumer products
  - Some are highly potent skin sensitizers/allergens
    - Methyisothiazolone (MI)/ chloromethyl isothiazolone (MCI) used in combination as Kathon CG
  - Increasingly being restricted in cosmetics and other products
  - Sensitization exposure limit for MCI is 1.9 mcg/cm^2 skin surface area



methyl chloroisothiazolinone (MCI)



methyl isothiazolinone (MI)

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Case Study

- Company produces consumer products of which leather wrist straps are one product option
  - New product models are rigorously tested for chemical leaching prior to release
- Testing reveals MI/MCI present in extracts of leather products
  - Most have acceptably low concentrations but a few fail and must be redesigned (at substantial time & cost)

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Case Study

- **Question:** Are there alternatives to MI/MCI in leather that we can propose to our suppliers?
- **Solution:** Conduct an IC2 Stage 1 AA to see what options are possible
- **Goal:** Be able to have an informed conversation with suppliers about possible options

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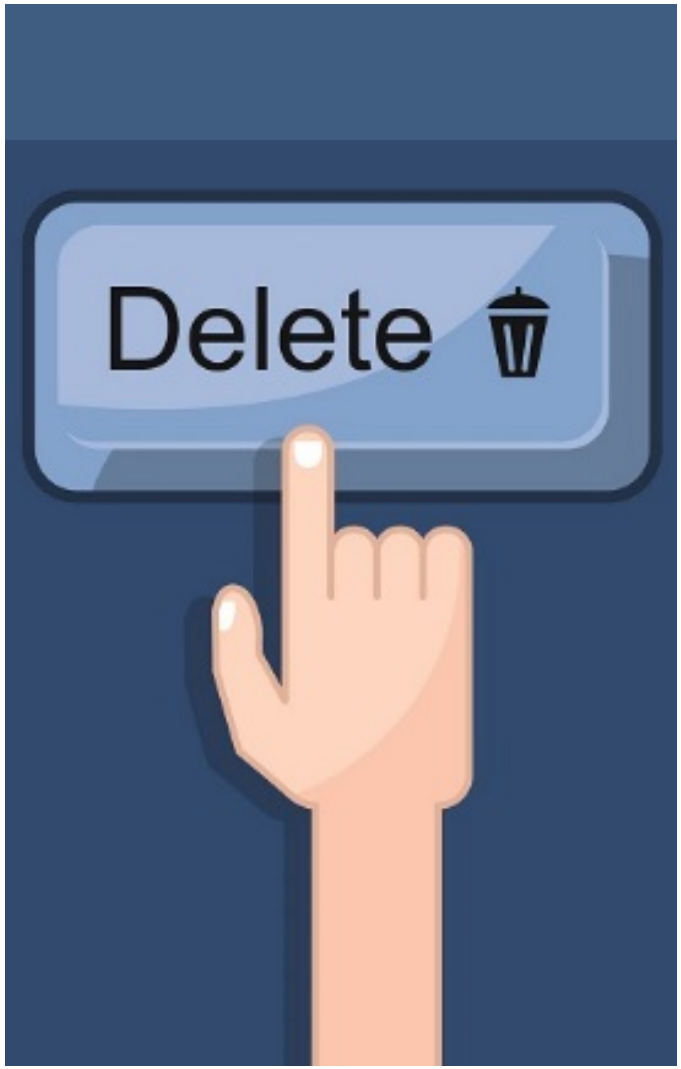
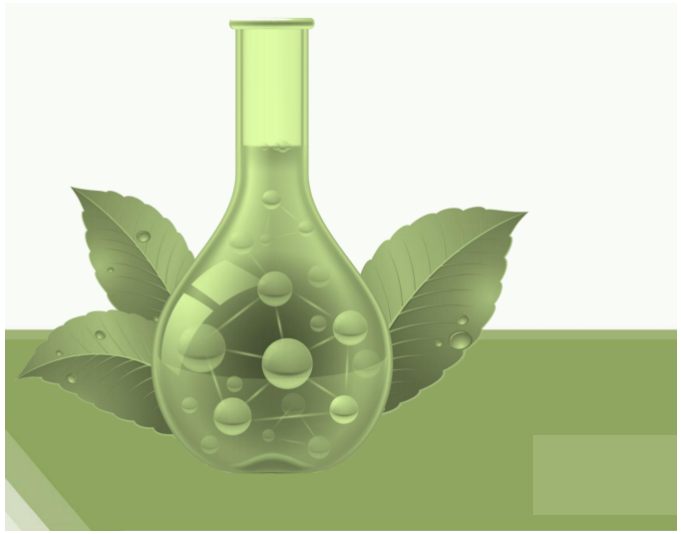
Initial AA Questions

- Can the chemical just be eliminated?
  - No. Due to the biological nature of leather, some antimicrobial is needed
- Can the company just avoid using leather?
  - No. Customers are asking for leather products.



Stage 1 IC2 AA Process

- High level review to see if data are available to support a more in-depth AA
- Limited to data that are readily available (no new research, no proprietary data)
- Modules: Hazard, Availability, Exposure, Performance, Cost
- Scope: Limited to alternatives actually in the market place



Process

- Identify Possible Biocides
- Being used/have been suggested for use in leather production or related processes
  - Manufacturer websites
  - Government reports
  - Journal articles
- Qualitative screen for Hazard, Exposure Potential, Performance, Availability and Cost
  - Pharos for hazard, EpiSuite for Phys/ Chem data, on-line searches for performance, availability and cost

Biocides With Documented Use in Leather Tanning or Related Materials or Processes

- Sodium- dimethyldithiocarbamate
- Potassium-dimethyldithiocarbamate
- Phenoxyethanol
- 2 (Thiocyano methylthio) benzothiazole (TCMBT); also referred to as TCMTB

Hazards of Alternatives (*via* Pharos)

	Common Chemical Name	Skin Sensitization	Carcinogenic	Mutagenic	Repro/ Developmental	Ecological	Other
Compounds of Concern	Methyl isothiazolinone (CAS 2682-20-4)	Skin sensitizer. POD =16.5 µg/cm^2	Not flagged	Not flagged	Not flagged	Yes (GHS Very Toxic)	Eye Irritation (NZ, A) Skin Irritation (A) Endocrine (TEDEX) Acute Inhalation (A) Respiratory Irritation (EU)
	Methylchloro isothiazolinone (26172-55-4)	Skin sensitizer. POD = 1.9 µg/cm^2	Not flagged	Not flagged	Not flagged	Yes (GHS Very Toxic)	Acute Inhalation (A) Eye Irritation (NZ, A) Skin Irritation (A)
Possible Alternatives	Sodium- dimethyl dithiocarbamate (128-04-1)	Possible sensitizer (structural alert). estimated POD = 250 µg/cm^2	Not flagged	Yes (GHS Cat 2)	Yes (GHS Cat 2, Prop65)	Yes (GHS Cat 1)	STOT Single (J) Acute Oral (NZ) Skin Irritation (J)21564-17-0
	Potassium-dimethyl dithiocarbamate (128-03-0)	Possible sensitizer (structural alert). estimated POD = 250 µg/cm^2	Not flagged	Yes (GHS Cat 2)	Yes (GHS Cat 2, Prop65)	Yes (GHS Very Toxic)	No other hazards flagged
	Phenoxyethanol (122-99-6)	Non-sensitizer	Not flagged	Not flagged	Yes (GHS Cat 2 but >375 mg/kg)	Yes (GHS Harmful)	Acute Oral (EU) Eye Irritation (EU) STOT Single (J)
	TCMBT (21564-17-0)	Skin sensitizer. POD = 25,000 µg/ cm^2	Not flagged	Not flagged	Yes (GHS Cat 2 but >125 mg/kg)	Yes (GHS Very Toxic)	Endocrine (TEDEX) Acute Inhalation (EU) Eye Irritation (EU) Skin Irritation (EU) STOT Single (NZ)

Results of Stage 1 AA

Common Chemical Name		Performance	Hazard	Availability	Comparative Exposure	Comparative Cost per ton
Compounds of Concern	Methylisothiazolinone (CAS 2682-20-4)	Demonstrated use	Skin sensitizer, not reprotoxic, aquatic toxicity	Readily available	Existing chemicals	Existing chemicals
	Methylchloro isothiazolinone (26172-55-4)	Demonstrated use	Skin sensitizer, not reprotoxic, aquatic toxicity	Readily available		
Possible Alternatives	Sodium dimethyl dithiocarbamate (128-04-1)	Used in leather process, ability to replace isothiazolones uncertain	Possible skin sensitizer, mutagenic, Prop65 Repro hazard, aquatic toxicity	Readily available	Less volatile, more hydrophillic	*Less*
	Potassium dimethyl dithiocarbamate (128-03-0)	Used in leather process, ability to replace isothiazolones uncertain	Possible skin sensitizer, mutagenic, Prop65 Repro hazard, aquatic toxicity	Readily available	Less volatile, more hydrophillic	*similar*
	Phenoxyethanol (122-99-6)	Used in textile processing, replacing isothiazolones in some consumer products	Not sensitizing, repro at high concentrations (>300 mg/kg), lowest aquatic toxicity	Readily available	Similar volatility, more hydrophobic	*similar*
	TCMBT (21564-17-0)	Marketed for use in leather process, ability to replace MI/MCI unknown	Not sensitizing, repro at high concentrations, endocrine active, aquatic toxicity	Readily available	Less volatile, more hydrophobic	*Substantially higher*

Note: Cost data are highly uncertain and represent cost of bulk material, not cost accounting for different antimicrobial potency (no data available)

Key Findings

- MI/CMI actually have some benefits over most alternatives
- Phenoxyethanol offers the best trade off between sensitization and other health hazards
  - Not clear it could be used in leather tanning
- TCMBT is non sensitizing and is being marketed for use in leather production
  - Cost could be substantially higher, depending on relative potency
  - Reported endocrine activity needs to be evaluated more closely
- Company should contact suppliers, get input and explore possibilities
- Depending on supplier input, conduct a 2nd Stage AA

Limitations

- There are other chemicals of concern in leather (chromium VI, acrylate or formaldehyde based adhesives) – are we targeting the key concern?
- Available cost data are of extremely poor quality, specific prices depend on volume and contracting
  - What really matters is cost for equivalent antimicrobial effect for which data could not be located
- Difficult for a small purchaser to put pressure on suppliers to research new options

Questions?

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