

Current Trends in Cosmetic Preservation

Linda B. Sedlewicz
Country Manager
schülke inc.

the plus of pure
performance

Topics

- Frequency of use
- Traditional preservatives
 - Parabens
 - Isothiazolinones
 - Formaldehyde & formaldehyde-donor
 - IPBC
 - Organic acids
- Non-traditional preservation methods
 - Glycols
 - Phenethyl alcohol
 - Ethylhexylglycerin
 - Chlorphenisin
 - Extracts & essential oils
 - Water Activity
 - Hurdle technology
- “Green”, “Natural”, “Sustainable”

Frequency of use

Top 10 Preservatives

(as per FDA registration)

	2007		2010	
Total Number of Formulations	27,771	% of total	36,811	% of total
Methylparaben/Sodium methylparaben	11881	42.78%	13899	37.76%
Propylparaben/Sodium propylparabe	9382	33.78%	10560	28.69%
Phenoxyethanol	5132	18.48%	8878	24.12%
Butylparaben	2784	10.02%	5289	14.37%
Ethylparaben	3789	13.64%	4869	13.23%
Isobutylparaben	1684	6.06%	2693	7.32%
Methylisothiazolinone	1409	5.07%	2408	6.54%
Methylchloroisothiazolinone/Methylisothiazolinone	1392	5.01%	2235	6.07%
DMDM Hydantoin	1665	6.00%	2035	5.53%
Imidazolidinyl urea	2266	8.16%	2007	5.45%

“2010 Frequency of Preservative Use”, David C. Steinberg,
Cosmetics & Toiletries Magazine, Dec. 2010

Frequency of use

Non-traditional / “Natural”

(as per FDA registration)

	2007		2010	
Total Number of Formulations	27,771	% of total	36,811	% of total
Caprylyl glycol	591	2.13%	1712	4.65%
Chlorphenesin	441	1.59%	1065	2.89%
Penethylene glycol		0.00%	705	1.92%
1,2 Hexandiol		0.00%	162	0.44%
Citrus grande (Grapefruit) seed extract	37	0.13%	108	0.29%
Phenethyl alcohol		0.00%	63	0.17%
Lactoperoxidase	19	0.07%	61	0.17%
Thymol		0.00%	14	0.04%
Climbazole	11	0.04%	13	0.04%
Hinokitiol	11	0.04%	11	0.03%

“2010 Frequency of Preservative Use”, David C. Steinberg,
Cosmetics & Toiletries Magazine, Dec. 2010

Traditional Preservatives

Parabens

- **Target Organisms**

- *Fungi*

- **Applications**

- *Rinse-off, leave-on*

- **Formulating Tips**

- *Low water solubility*
- *Inactivated by nonionics, ethoxylates*

- **pH Range**

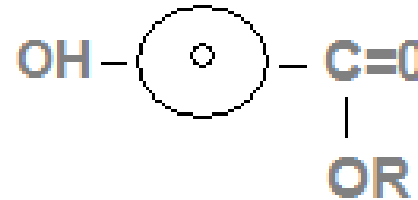
- *3.5-6.5 pH (optimal)*
- *Can be used up to pH 8*

- **Use Level**

- *0.1-0.8%*
- *approved in Japan up to 1.0%, EU and Brazil up to 0.8% total paraben; additional restrictions for single parabens*

Structure Example

General paraben functionality



Comments

- Major Types: methyl, propyl, butyl, ethyl
- Most widely used preservatives in the world
- Currently under discussion – estrogenic effect re: breast cancer, male reproductive system
- SCCS – methyl, ethyl “Safe as Used”; others “not enough information”

In vitro, parabens exhibit weak estrogenic activity (Routledge et al., 1998)

- Methyl-, ethyl-, propyl-, and butylparaben exhibited potencies that were respectively *1/2,500,000th, 1/150,000th, 1/30,000th, and 1/10,000th that of estradiol-17 β*

Darbre et al. (2004) detected parabens in breast cancer tissue obtained from 20 patients

- Study did not include paraben levels in normal breast controls
- Prevalent paraben detected was methylparaben, devoid of estrogenic activity
- The most estrogenic (propyl-, butyl-, and isobutyl-) parabens are estimated to be about 15 ng/g (or 0.1 μ M), below bioactive levels
- Paraben estimates may have been flawed (blanks were high)
- Concerns expressed about medical histories of subjects

Endocrine Disruption and Personal Care Products
R. J. Witorsch, Ph.D., et al
PCPC webinar, July 21 2010

Parabens

December 2010 -The use levels recommended by the SCCS are:

- Methylparaben: 0.4% (acid)
- Ethylparaben: 0.4% (acid)
- Propylparaben, Butylparaben: 0.19% individually or in combination

December 2010 - Denmark issued a request to ban all parabens in children's products under the age of 3.

October 2011 – SCC clarification on their position on parabens

“For general cosmetic products containing parabens, excluding specific products for the nappy area, the SCCS considers that there is no safety concern in children (any age group) as the MOS was based on very conservative assumptions...”

“for application on the nappy area, a risk cannot be excluded...” More data needed
(Clarification on Opinion SCCS/1348/10)

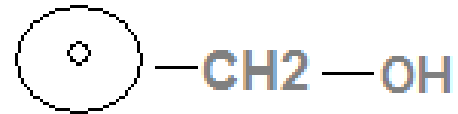
May 2011 – French National Assembly has passed a ban on parabens in consumer products. French Senate vote not yet scheduled.

Alcohols

- **Target Organisms**
 - *Bacteria*
- **Applications**
 - *Rinse-off, leave-on*
- **Formulating Tips**
 - *Highly water soluble*
 - *May have characteristic odor*
- **pH Range**
 - *3-10 pH*
- **Use Level**
 - *0.5-1.0%*
 - *Approved globally, including Japan*

Structure Example

General alcohol functionality



Comments

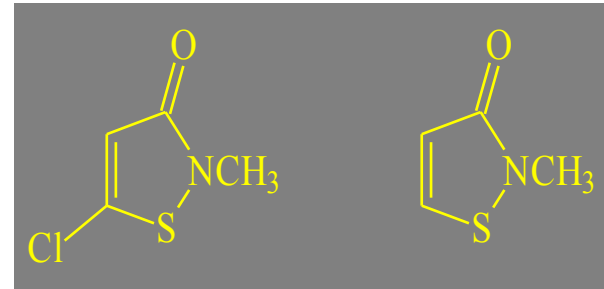
- Major Types: phenoxyethanol, benzyl alcohol, ethyl alcohol
- Phenoxyethanol had been of concern in France. Formally approved up to 1.0%, but still some manufacturers have reservations.
- Benzyl alcohol listed as a fragrance allergen in Europe

Isothiazolinones

- **Target Organisms**
 - *Bacteria and Fungi*
- **Applications**
 - *Mainly rinse-off*
- **Formulating Tips**
 - *Most common blend is CMI / MI*
 - *Sensitization issues*
- **pH Range**
 - *2-8 pH*
- **Use Level**
 - *Typically 1.5% active solution – 3:1 blend*
 - *CIR max. 15 ppm rinse-off*
 - *CIR max 7.5 ppm leave-on*
 - *EU max. 15 ppm*
 - *Japan rinse-off only*
 - *max. 100 ppm MI*

Structure Example

CMI/MI



Comments

- Major types: chloromethylisothiazolinone, methylisothiazolinone
- Not widely accepted in Germany and Scandinavia
- CMI/MI approved for use in Japan for rinse-off only
- MI approved for use in Japan for leave-on and rinse-off, except mucous membrane

Formaldehyde & Formaldehyde-donors

- **Target Organisms**

- *Bacteria*

- **Applications**

- *Leave-on, rinse-off*

- **Formulating Tips**

- *Highly water soluble*
- *Temperature sensitive*

- **pH Range**

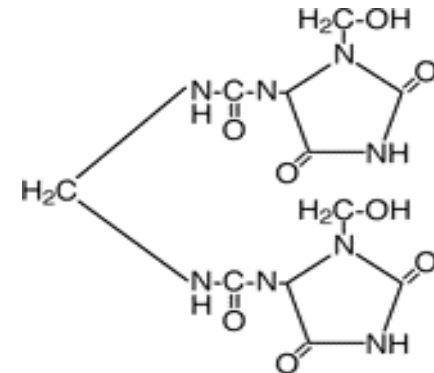
- *3-10 pH*

- **Use Level**

- *0.1-0.5%*
- *Warning label required in Japan*

Structure Example

Imidazolidinyl urea



Comments

- Major Types: imidazolidinyl urea, diazolidinyl urea, DMDM hydantoin, sodium hydroxymethylglycinate, quaternium-15
- React with avobenzone
- Not well liked in some European countries
- Carcinogenicity???

Carcinogenicity

- Formaldehyde gas shown to be carcinogenic by inhalation (construction industry)
- “Prior editions of the RoC had listed formaldehyde as *reasonably anticipated to be a human carcinogen*, and following a rigorous scientific review, formaldehyde is now reassigned to the category *known to be a human carcinogen*.” – National Toxicology Program, US Dept. HHS, *Addendum to the 12th Report on Carcinogens*
- Formaldehyde-donors in formulation produce formalin (aqueous)
- Formalin has not been shown to be carcinogenic
- Methylene glycol approved as INCI name

- **Target Organisms**

- *Fungi*

- **Applications**

- *Rinse-off, leave-on*

- **Formulating Tips**

- *Low water solubility*
- *Inactivated by reducing agents, alkaline pH's*

- **pH Range**

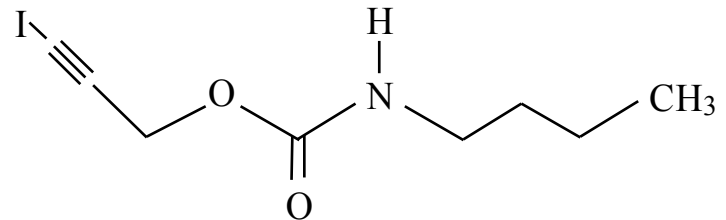
- *Up to 9 pH*

- **Use Level**

- *0.05-0.1% as active*
- *Approved in Japan to 200 ppm*
- *Restriction on use in EU*

Structure Example

Iodopropynyl butyl carbamate



Comments

- Available in surfactant, water or bicarbonate solid
- 100% active not often sold due to discoloration and clumping
- Solutions may darken over time and/or at elevated temperature

European Union Restrictions

- **Not to be used in oral and lip products**
- **Rinse-off products up to 0.02%**
 - Not to be used in products for children under 3 years of age, except in bath products/ shower gels and shampoo
- **Leave-on products up to 0.01%**
 - Not to be used in body lotion and body cream
 - Not to be used in products for children under 3 years of age
- **Deodorants & Antiperspirants up to 0.0075%**

REGULATION (EC) No 1223/2009 OF THE EUROPEAN
PARLIAMENT AND OF THE COUNCIL
of 30 November 2009
on cosmetic products

Organic Acids

- **Target Organisms**

- *Fungi*

- **Applications**

- *Rinse-off, leave-on*

- **Formulating Tips**

- *Acid forms have low water solubility*
- *Only the free acids active*
- *Use in combinations*

- **pH Range**

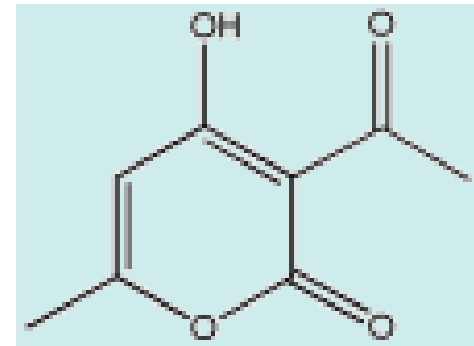
- *<6 pH or lower depending on acid*

- **Use Level**

- *Typically, up to 0.5% as the free acids*
- *Approved globally, including Japan*

Structure Example

Dehydroacetic acid



Comments

- Main types: sorbic, benzoic, salicylic, dehydroacetic, citric
- Salts often used for better water solubility
- Extremely pH dependant

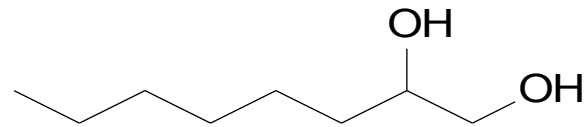
Non-traditional Preservation Methods

Glycols

- **Target Organisms**
 - *Bacteria, weak against fungi*
- **Applications**
 - *Rinse-off, leave-on*
- **Formulating Tips**
 - *Synergistic effects when combined*
 - *High levels can cause eye area stinging*
- **pH Range**
 - *2-10 pH*
- **Use Level**
 - *1-5%*
 - *Approved globally, including Japan*

Structure Example

Caprylyl glycol



Comments

- Main types: pentylene glycol, caprylyl glycol, 1,2-hexanediol
- Limiting factor - water solubility
- Caprylyl glycol – recent CIR review “Safe as used”

Phenethyl alcohol

- **Target Organisms**

- *Bacteria, weak against fungi*

- **Applications**

- *Rinse-off, leave-on*

- **Formulating Tips**

- *Reacts with oxidizers, include antioxidant in formula*
- *Inactivated by nonionics*

- **pH Range**

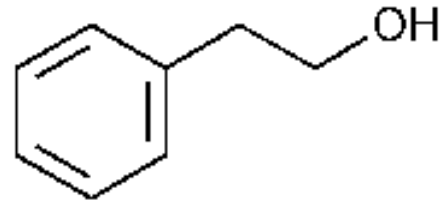
- *Best at acid pH*

- **Use Level**

- *Up to 1%*
- *Approved globally, including Japan*
- *Limited to 0.5% as preservative in Argentina; Allowed as fragrance*
- *Allowed as fragrance in Brazil*

Structure Example

Phenethyl alcohol



Comments

- Strong rose odor
- Not listed as preservative in EU or Japan
- GRAS for food use
- Used to preserve eye drops
- Natural source available - (~10x price of synthetic)

Ethylhexylglycerin

- **Target Organisms**

- *Gram positive bacteria; yeast & mold at higher use levels*

- **Applications**

- *Leave-on, some rinse-off*

- **Formulating Tips**

- *Limited water solubility*
- *Booster for traditional and non-traditional preservatives*
- *HLB 7.5*

- **pH Range**

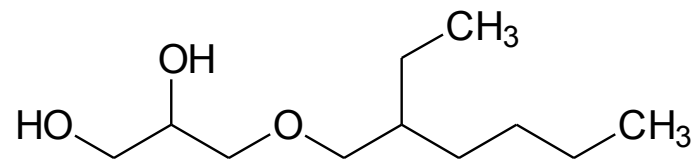
- *2-12 pH*

- **Use Level**

- *0.1-1%*
- *Approved globally, including Japan*

Structure Example

Ethylhexylglycerin



Comments

- Deodorant active
- Can destabilize emulsions - HLB
- Eye area stinging if used with high levels of glycols
- Emollient
- Determined "Safe-as-Used" by CIR

Chlorphenisin

- **Target Organisms**

- *Fungi*

- **Applications**

- *Rinse-off, leave-on*

- **Formulating Tips**

- *Limited water solubility*
- *Best with high levels of silicone*

- **pH Range**

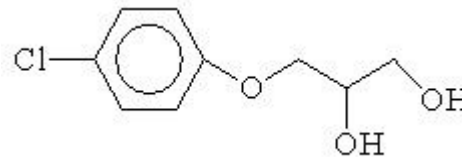
- *Best at acid pH*

- **Use Level**

- *Up to 0.3%*
- *Approved globally, including Japan*
- *Limited to 0.3% in EU, Japan and Brazil*
- *Not permitted for mucous membrane in Japan*

Structure Example

Chlorphenesin



Comments

- Mainly used to boost traditional and non-traditional preservation systems
- Powder, easiest to dissolve in glycerin, glycol or >50° water

Extracts & Essential Oils

- **Target Organisms**

- *Organism specific*

- **Applications**

- *Rinse-off, leave-on*

- **Formulating Tips**

- *Need to be blended for broad spectrum effect*

- **pH Range**

- *Varied*

- **Use Level**

- *Usually high use level to be effective*

Comments

- Often strong odor and/or color at effective use levels
- May have high level of irritation or sensitization at use level
- Some listed on EU Allergens List

Water Activity (A_w)

- Measure of water available to support microbial growth
- Not directly related to % water in formula
- Must be measured, not calculated
- Different organisms grow at different A_w

pH

- Different organisms survive best at different pH
- pH may affect the efficacy of some preservatives

Aw and pH limits and product types

Table I
Water Activity and the Potential for Growth

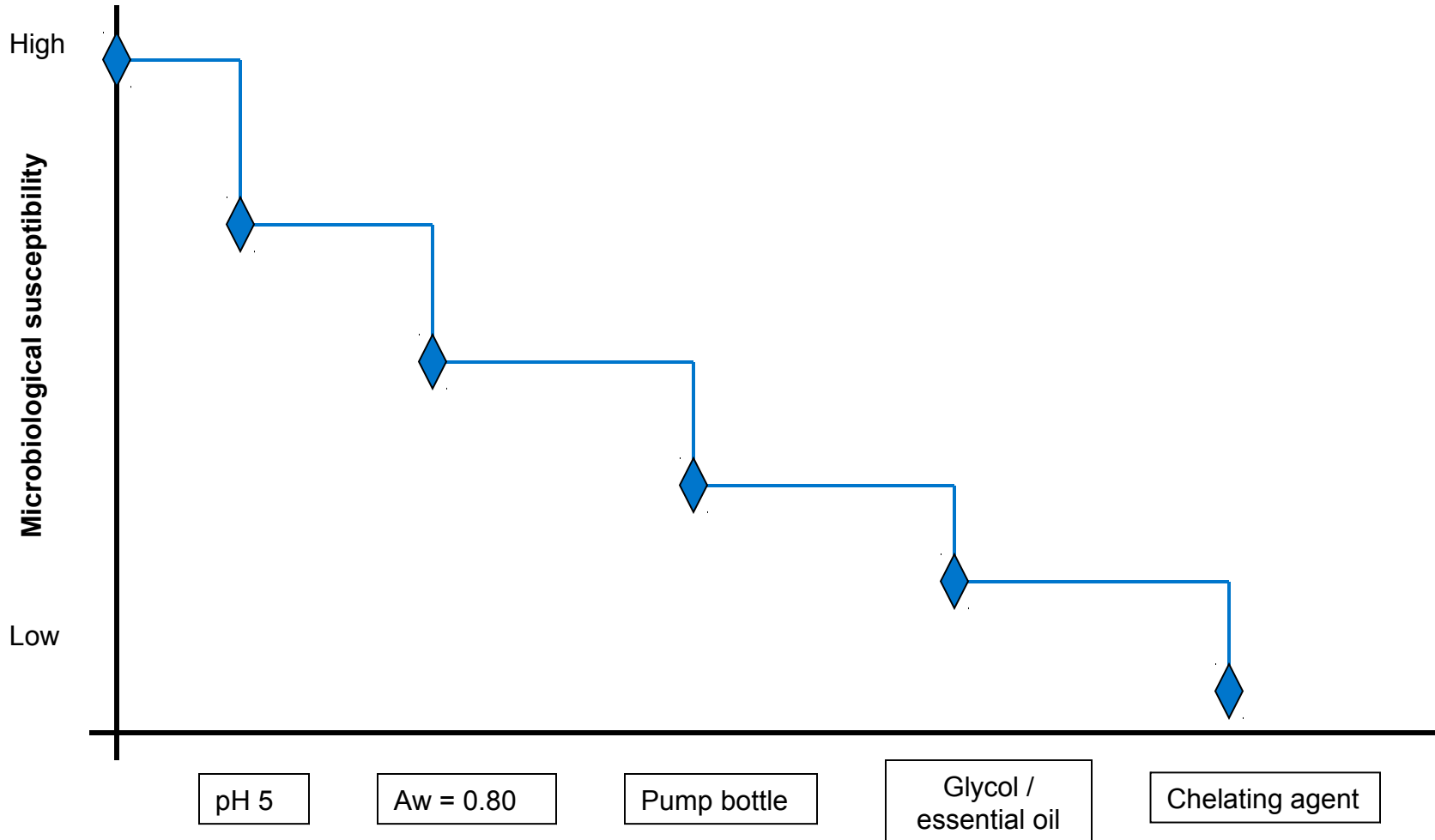
Water activity	pH	Problem organisms capable of growth	Examples of cosmetic products
0.98–1.00	pH 5–9	Most Gram positives and negatives	Shampoos and emulsion products
0.95–0.97	pH 5–9	Most Gram positives and negatives (<i>Pseudomonas</i> begins to be limited)	Liquid make-ups and eye area products
	Below 5.5	Some Gram negatives and most Gram positives (<i>Pseudomonas</i> limited)	Some hair conditioners
0.92–0.95	Above 5.5	Few Gram negatives and most Gram positives	Some pressed powders
	Below 5.5	Most Gram positives	
0.90–0.92	pH 5–9	Gram positive Lactobacilli and <i>Staph.</i>	Some rouges (non-water based)
0.80–0.90	pH 5–9	<i>Staph.</i> , molds, yeasts	Lipsticks (non-water based)
0.70–0.80	pH 5–9	Molds, yeasts	Some talcs
0.65–0.70	pH 5–9	Osmotolerant yeasts	Some antiperspirants
0.60–0.70	pH 5–9	Osmotolerant and xerophilic molds	
Below 0.60	pH 5–9	None	

Brannan, D. K., (July/August 1995). *Cosmetic Preservation. J. Soc. Cosmet. Chem.*, 46, 199-220

Hurdle Technology

The use of a variety of methods (chemical, physical, traditional, non-traditional) to reduce the microbiological susceptibility of a product.

Hurdle Technology



“Green”, “Natural”, “Sustainable”

“Green”, “Natural”, “Sustainable”

What is “green”, “natural”, “sustainable”?

- Different definitions
- Many certification bodies, all with different criteria – Natural Products Association, Oasis, EcoCert, NaTrue, Soil Association
- Shift “natural” → “green” → “sustainable”

“Green”, “Natural”, “Sustainable”



Meaty Matters
Lab-grown meat emerges as the big winner in a study comparing its environmental impact to that of meat from conventionally raised animals. Researchers have calculated that cultured meat has a smaller environmental footprint than do beef, sheep, pork, and poultry.

cenm.ag/env44

Chemical & Engineering News, July 4, 2011

“Green”, “Natural”, “Sustainable”

“Sustainable”

- Produced with minimal impact on the environment
- Preferably natural/organic
- Synthetics allowed if:
 - Proven safe
 - Low environmental impact production
 - Biodegradable
 - Preservation methods, if comply with above
 - ★ Phenoxyethanol
 - ★ Caprylyl glycol
 - ★ Ethylhexylglycerin
 - ★ Organic acids
 - ★ Chelating agents
 - ★ Etc.

“Green”, “Natural”, “Sustainable”

“P&G research has shown us that around 70% of consumers around the world want more environmentally friendly products, but they’re not willing to compromise on performance, aesthetics or value.”

Jenny Rushmore, global sustainability leader for P&G Beauty & Grooming.
“Sustainable Innovation,” GCI December 2010

“Green”, “Natural”, “Sustainable”

“While there is a place in the market for ultra natural brands that avoid surfactants emulsifiers and preservatives, there simply are not enough consumers willing to do without traditional beauty products.”

“According to Sundale Research, natural and organic products are expected to account for 17.4% of the beauty industry by 2013, up from the 5.1% expected in 2010.”

“Gaining Consumer Confidence by Finding Common Ground, Kayla Fioravanite, GCI June 2010

What's next?



Consumer perception

Marketing driven

Regulatory driven

Focus on non-traditional preservation methods

Preservation choice must be part of the overall product concept!

Questions!