The future availability of preservatives

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Preservation of Paints & Detergents: Workshop on Innovation & Industry challenges
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www.aise.eu  www.cepe.org
Agenda

Part I
1. Green Steps
2. Why do we need preservatives?

Part II
1. Future availability of biocides for PT6 and PT7 are at risk
2. Concerns
Green Steps

• Solvent borne products changed to water borne products → significant reduction of VOC emissions
• Shift from powder detergents to liquid detergents → significant reduction in energy consumption
• Continuous R&D work to substitute, optimize and reduce concentrations of biocides
• Informed labelling that goes beyond the legal requirement

Strict and highly conservative decisions under BPR will counteract Green Steps!
Where there is water there is life
Microorganisms have low nutrient requirements and adapt easily
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Microorganisms have low nutrient requirements and adapt easily
Microorganisms to control

**Bacteria**
e.g. *Pseudomonas* spp., *Bacillus* spp.

**Yeast (Fungi)**
e.g. *Saccharomyces* spp., *Candida* spp.

**Fungi (Mould)**
e.g. *Alternaria* spp., *Penicillium* spp.

**Algae**
e.g. *Stichococcus* spp., *Klebsormidium* spp.

In the can (PT6): Bacteria, yeast and fungi
On the surface (PT7): Fungi and algae
There is no “one solution fit all”

- pH
- Temperature
- Incompatibility (e.g. deactivation due to oxidizing agents, reducing agents, nucleophilic substances, electrophilic substances, hydrolysis)
- Fast and slow acting biocides
- Stability (e.g. demand for 2 years shelf life of consumer products)
- Protection gaps (e.g. BIT and *Pseudomonas* spp. IPBC and *Alternaria* spp.)

There is no “one solution fit all” - we need several active ingredients to ensure successful preservation of all water borne products!
Successful preservation

Requirements for successful preservation: (1) OK microbiological quality of raw materials, (2) effective plant hygiene, and (3) adequate product preservation.
Combined effects allow lower dose

Table 22  Minimum inhibitory concentrations of 2-methyl-4-isothiazolin-3-one

<table>
<thead>
<tr>
<th>Organism</th>
<th>MIT (ppm)</th>
<th>BIT (ppm)</th>
<th>MIT/BIT (1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Escherichia coli</em></td>
<td>17.5</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td><em>Klebsiella pneumoniae</em></td>
<td>20</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td><em>Proteus vulgaris</em></td>
<td>25</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>30</td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td><em>Pseudomonas putida</em></td>
<td>12.5</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td><em>Pseudomonas stutzeri</em></td>
<td>12.5</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td><em>Aspergillus niger</em></td>
<td>750</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td><em>Paecilomyces variotii</em></td>
<td>100</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td><em>Penicillium funiculosum</em></td>
<td>200</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae</em></td>
<td>150</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

Please note this is a lab test. Successful preservation levels are higher in real life.
Tolerance and resistance to biocides

Tolerance/resistance typically occurs when microorganisms are:

- Exposed to a single active ingredient
- Exposed to sub-lethal doses of active ingredients

Table 1 Summary of increase in MICs for R2A and CDM media

<table>
<thead>
<tr>
<th>Biocide</th>
<th>Medium</th>
<th>MIC (µg ml⁻¹) for passage number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>BIT</td>
<td>R2A</td>
<td>56</td>
</tr>
<tr>
<td>MIT</td>
<td>R2A</td>
<td>19</td>
</tr>
<tr>
<td>CMIT</td>
<td>R2A</td>
<td>1.3</td>
</tr>
<tr>
<td>thiomersal</td>
<td>R2A</td>
<td>9.4</td>
</tr>
<tr>
<td>BIT</td>
<td>CDM</td>
<td>5.73</td>
</tr>
<tr>
<td>MIT</td>
<td>CDM</td>
<td>2.46</td>
</tr>
<tr>
<td>CMIT</td>
<td>CDM</td>
<td>0.25</td>
</tr>
<tr>
<td>thiomersal</td>
<td>CDM</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND – not done. Passage 1 indicates the original pre-exposure MIC.

Source: C.L. Winder et al. Journal of Applied Microbiology, 89, 289-295
Tolerance and resistance to biocides

Mechanisms involved in tolerance/resistance include:

- **Shift in the outer membrane protein** (i.e. the biocide will not be able to enter the bacteria and exert its effect)

- **Bacterial efflux pump** (i.e. moving biocides out of the bacterial cell preventing the biocide from performing its effect)
Damages caused: Wet-state

- Unpleasant smell
- Discoloration
- Gas formation
- pH-drift
- Change in viscosity
- Visible microbial growth

Destruction of the product ingredients and loss of product function/efficiency

WASTE
Damages caused: Dry-film

- Aesthetical problem
- Damage of the coating and substrate
- Shorter service life and increased use of non-renewable materials
- Decrease property value
Summary part I

- Microorganisms are everywhere: Low nutrient requirements and adapt easily
- Biocides are essential for water borne products and exterior paints
- No “one solution fits all”: different chemistries require different biocides
- Active ingredients should be combined: allows reduced doses and reduce the risk of resistance
The future is uncertain for essential biocides!

- Lack of holistic approach
- Exclusion criteria
- Low SCL for isothiazolinones

**PT6 in-can preservatives on the Article 95 list:**
52 active ingredients on the list
15 are compatible in paint, printing ink – not enough options the future (DIY)!
10 are compatible in detergents – not enough options for the future!

**PT7 dry film preservatives on the Article 95 list:**
31 active ingredients on the list
10 are compatible in paint – not enough options the future (DIY)!
# Concerns for isothiazolinones

<table>
<thead>
<tr>
<th>Active substance</th>
<th>Application</th>
<th>Typical dosage (ppm)</th>
<th>Concern for future availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIT/MIT</td>
<td>Bactericide (PT6)</td>
<td>15-30</td>
<td>SCL is 15 ppm</td>
</tr>
<tr>
<td>MIT</td>
<td>Bactericide (PT6)</td>
<td>100</td>
<td>New SCL is 15 ppm (1 May 2020)</td>
</tr>
<tr>
<td>MBIT</td>
<td>Bactericide (PT6)</td>
<td>100-300</td>
<td>Proposed SCL is 15 ppm</td>
</tr>
<tr>
<td>BIT</td>
<td>Bactericide (PT6)</td>
<td>100-300</td>
<td>Expected SCL is 15 ppm</td>
</tr>
<tr>
<td>OIT</td>
<td>Fungicide (PT6 and PT7)</td>
<td>500-1000</td>
<td>Proposed SCL is 15 ppm</td>
</tr>
<tr>
<td>DCOIT</td>
<td>Fungicide (PT7)</td>
<td>1000-2000</td>
<td>Proposed SCL is 15 ppm</td>
</tr>
</tbody>
</table>
Concern that CIT/MIT will set precedence!

COMMISSION IMPLEMENTING REGULATION (EU) 2016/131
of 1 February 2016

approving C(M)IT/MIT (3:1) as an existing active substance for use in biocidal products for product-types 2, 4, 6, 11, 12 and 13

(Text with EEA relevance)

The placing on the market of treated articles is subject to the following conditions:

(1) In view of the risks identified for human health, mixtures treated with or incorporating C(M)IT/MIT (3:1) and placed on the market for use by the general public shall not contain C(M)IT/MIT (3:1) at a concentration triggering classification as skin sensitisers, unless exposure can be avoided by other means than the wearing of personal protective equipment.

(2) In view of the risks identified for human health, liquid detergents treated with or incorporating C(M)IT/MIT (3:1) and placed on the market for use by professional users shall not contain C(M)IT/MIT (3:1) at a concentration triggering classification as skin sensitisers, unless exposure can be avoided by other means than the wearing of personal protective equipment.
## Concerns for other essential biocides

<table>
<thead>
<tr>
<th>Active substance</th>
<th>Application</th>
<th>Typical dosage (ppm)</th>
<th>Concern for future availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnPT</td>
<td>Bactericide and fungicide (PT6 and PT7)</td>
<td>100-300/1000-5000</td>
<td><strong>Exclusion criteria</strong></td>
</tr>
<tr>
<td>NaPT</td>
<td>Bactericide (PT6)</td>
<td>100-300</td>
<td>Risk of the same classification as ZnPT?</td>
</tr>
<tr>
<td>Formaldehyde releasers</td>
<td>Bactericide (PT6)</td>
<td>200-400</td>
<td><strong>Exclusion criteria</strong></td>
</tr>
<tr>
<td>Bronopol</td>
<td>Bactericide (PT6)</td>
<td>200-400</td>
<td>Not compatible in all products: yellowing</td>
</tr>
<tr>
<td>IPBC</td>
<td>Fungicide (PT6 and PT7)</td>
<td>2000-5000 (PT7)</td>
<td>Not compatible in all products: yellowing and tear gas</td>
</tr>
<tr>
<td>Carbendazim</td>
<td>Fungicide (PT7)</td>
<td>1000</td>
<td>Only approved for industrial use. <strong>Exclusion criteria.</strong></td>
</tr>
<tr>
<td>Diuron</td>
<td>Algicide (PT7)</td>
<td>1000-2000</td>
<td><strong>Exclusion criteria?</strong> WFD, listed as priority substance</td>
</tr>
<tr>
<td>Terbutryn</td>
<td>Algicide (PT7)</td>
<td>1000-2000</td>
<td>WFD, listed as priority substance</td>
</tr>
<tr>
<td>Isoproturone</td>
<td>Algicide (PT7)</td>
<td>2000</td>
<td>Stop of support under PPR. WFD, listed as priority substance</td>
</tr>
</tbody>
</table>
The future for biocides is uncertain!

- Will there be a ban of preserved products?
- Will there be enough options for safe preservation of products?
Summary part II

• Only a few PT6 and PT7 biocides are compatible in paint, artist colors, printing ink and detergents

• There will be even less biocides in near future and no new ones are expected

• Liquid paints and detergents will be banned for consumers?
Thank you for your attention!