



The future availability of preservatives

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Preservation of Paints & Detergents: Workshop on Innovation & Industry challenges
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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





Microorganisms have low nutrient requirements and adapt easily





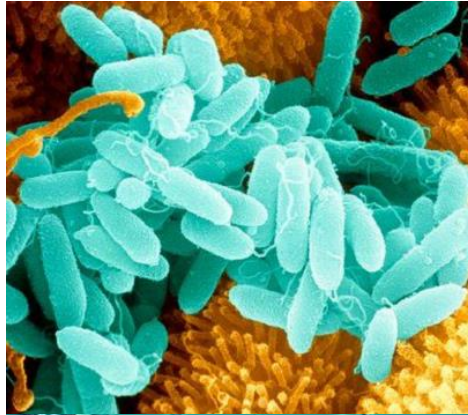
Microorganisms have low nutrient requirements and adapt easily



Microorganisms to control

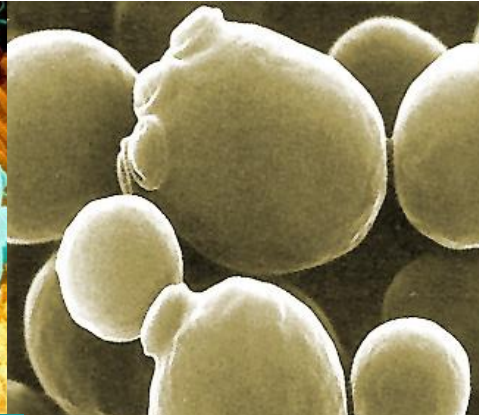
Bacteria

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”

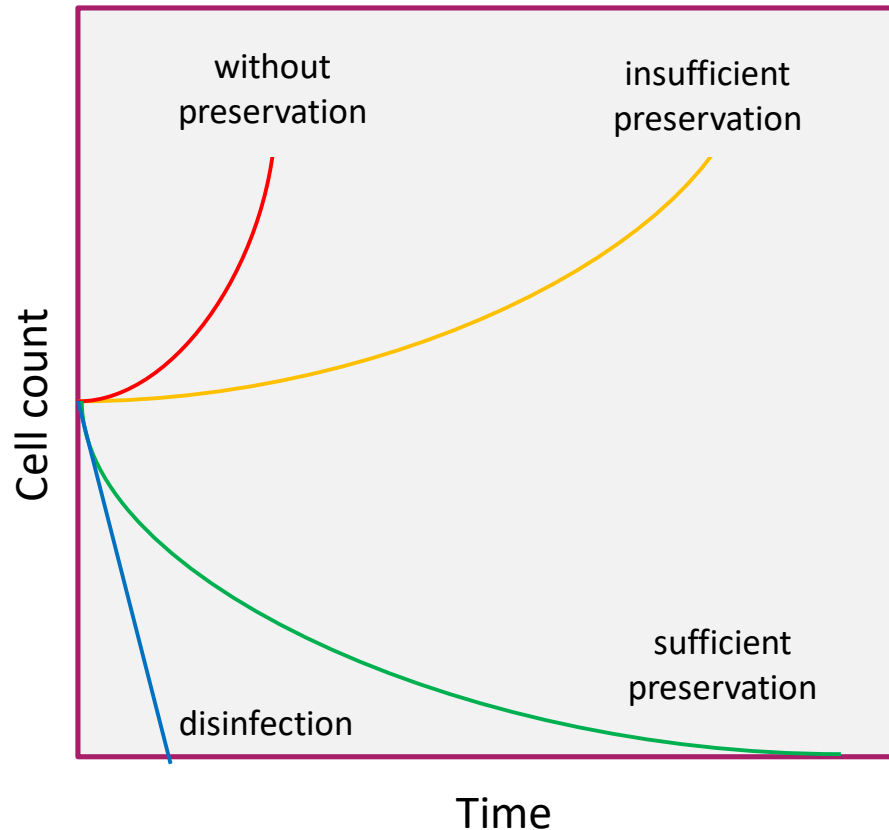
- pH
- Temperature
- **Incompatibility** (e.g. deactivation due to oxidizing agents, reducing agents, nucleophilic substances, electrophilic substances, hydrolysis)
- **Fast and slow acting biocides**
- **Stability** (e.g. demand for 2 years shelf life of consumer products)
- **Protection gaps** (e.g.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

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

Source: *Microbicides for the Protection of Materials: A Handbook*. W. Paulus.
 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

Biocide	Medium	MIC ($\mu\text{g ml}^{-1}$) for passage number	
		1	11
BIT	R2A	56	98.6
MIT	R2A	19	48.7
CMIT	R2A	1.3	2.5
thiomersal	R2A	9.4	17.93
BIT	CDM	5.73	9.07
MIT	CDM	2.46	9.8
CMIT	CDM	0.25	0.6
thiomersal	CDM	ND	ND

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

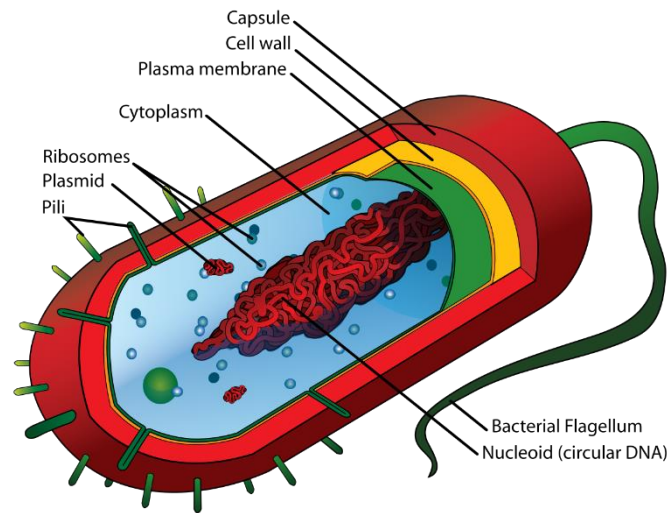
Source: C.L. Winder et al. *Journal of Applied Microbiology*, 89, 289-295



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

Active substance	Application	Typical dosage (ppm)	Concern for future availability
CIT/MIT	Bactericide (PT6)	15-30	SCL is 15 ppm
MIT	Bactericide (PT6)	100	New SCL is 15 ppm (1 May 2020)
MBIT	Bactericide (PT6)	100-300	Proposed SCL is 15 ppm
BIT	Bactericide (PT6)	100-300	Expected SCL is 15 ppm
OIT	Fungicide (PT6 and PT7)	500-1000	Proposed SCL is 15 ppm
DCOIT	Fungicide (PT7)	1000-2000	Proposed SCL is 15 ppm





Concern that CIT/MIT will set precedence!

L 25/48

EN

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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 sensitiser, 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 sensitiser, unless exposure can be avoided by other means than the wearing of personal protective equipment.



Concerns for other essential biocides

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





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?





Reducing energy consumption

Reducing carbon footprint

Reducing hazardous materials

Reducing VOC emissions

Reducing waste





Thank you for your attention!

