

# Identity, grouping and characterisation of silver based biocidal active substances including nano-silver

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# Identity, grouping and characterisation of silver based biocidal active substances including nano-silver

- What are biocides?
- The evaluation of silver under the biocides legislation
- Applications of biocidal silver
- Treated articles and their implications for risk assessment
- When is nano an issue?

# What are Biocides?



BIOCI

ANTI - MOLD FORMULA



No More  
MOLD



Effective  
Against  
PATHOGENIC  
FUNGI

ANTI - MOLD



# What are Biocides?



# What are Biocides?

- Biocides are agents usually meant to kill organisms
- They must not be sold without pre-marketing approval = authorization.
- Details are regulated in the European Biocides Directive (98/8/EC) respectively in the Biocides Regulation (Reg. EC No xxxx/2012) → to be published in summer 2012

# The evaluation of silver

- Silver is a potent antimicrobial agent
- Silver is used as **active substance** in *biocidal products* and in *treated articles*
- All **active substances** have to be *authorized* to be permitted to be placed on the market after May 2014

# The evaluation of silver

- Kemi (SE) is responsible for the evaluation of silver as an active substance within BPD
- At the moment: transitional period = unregulated market
- In future: only silver uses which show acceptable risks get authorized



# Silver?



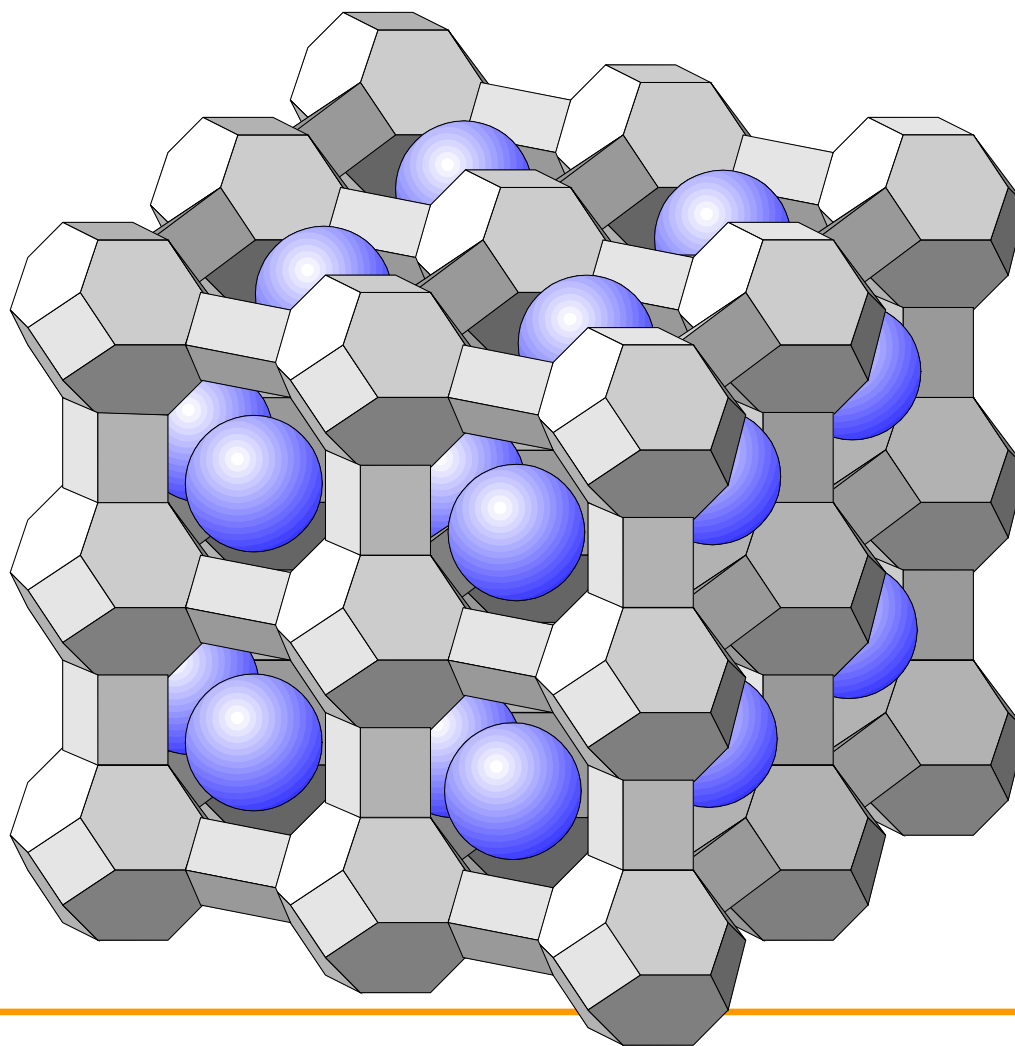
FOTOMONTAGE BY WILMA WHITE



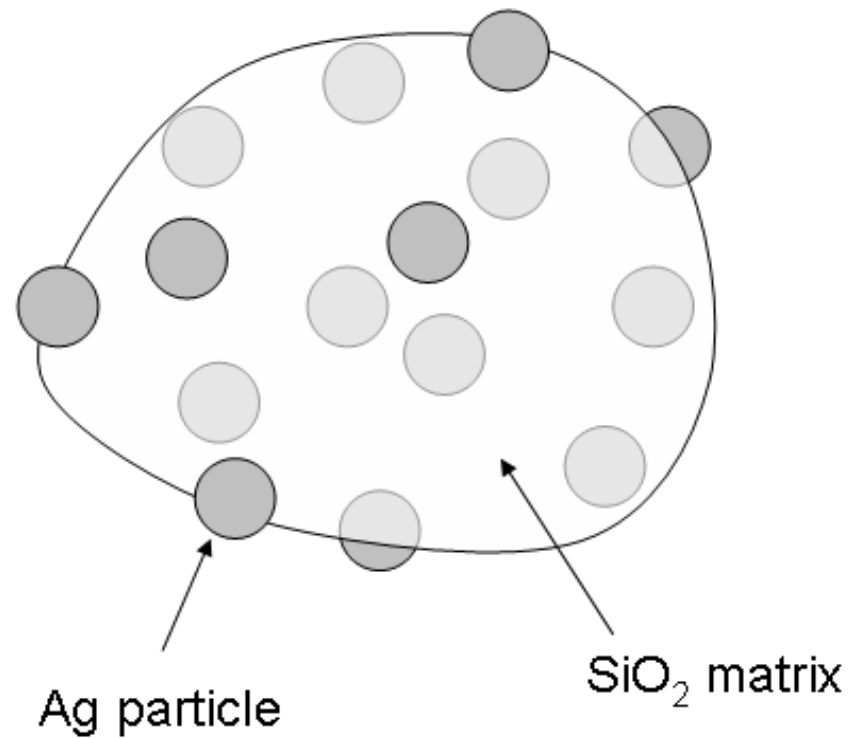
# Silver?

<b>Silver containing substance (SCAS)</b>		<b>CAS No.</b>
Elemental silver	a) Particulate silver	7440-22-4
	b) Silver ionisation systems	7440-22-4
<i>Silver adsorbed to silica dioxide</i>		<i>Not yet allocated</i>
<i>Silver chloride adsorbed to titan dioxide</i>		<i>Not yet allocated</i>
Silver nitrate		7761-88-8
Silver sodium hydrogen zirconium phosphate		265647-11-8
Silver zinc zeolite		130328-20-0
Silver copper zeolite		130328-19-7
Silver phosphate glass		308069-39-8
Silver borosilicate glass		308062-97-7

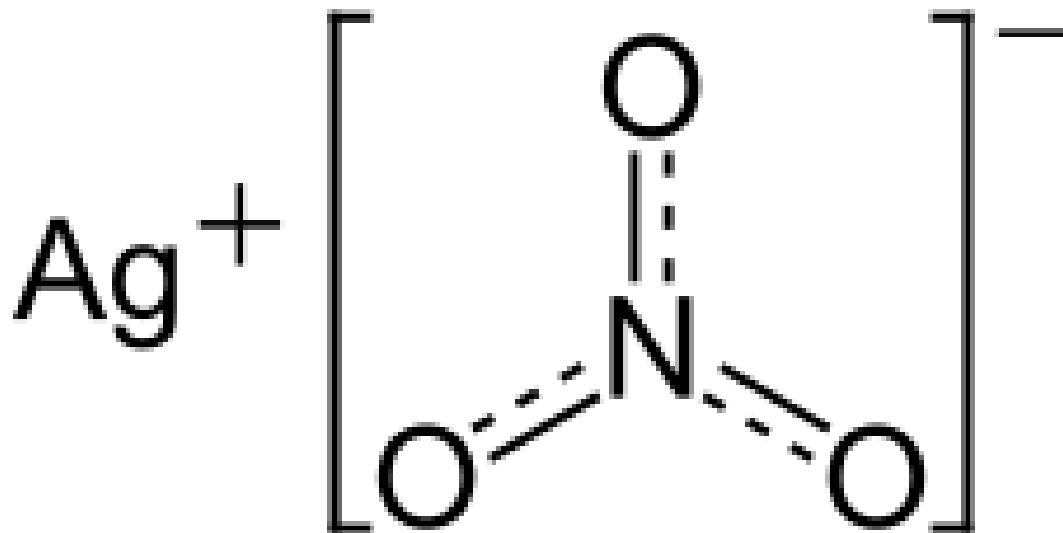
# Example: Silver (zinc) zeolite



# Example: Nano-silver composite



# Example: Silver nitrate



# Nano-Silver: Definition

## Biocides Regulation (from COM recommendation)

Art. 3, (z) "nanomaterial" means *a natural or manufactured active substance or non-active substance containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm; ...*

*For the purposes of the definition of nanomaterial, 'particle', 'agglomerate' and 'aggregate' are defined as follows:*

- (a) 'particle' means a minute piece of matter with defined physical boundaries;*
- (b) 'agglomerate' means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components;*
- (c) 'aggregate' means a particle comprising of strongly bound or fused particles;*

# Nano-Silver: Definition

## ***“Nano definition is lawyers' paradise, says expert***

A member of the UK government's Advisory Committee on Hazardous Substances (ACHS) has described the EU definition of nanomaterials adopted last October as a "lawyers' paradise" that will be difficult for regulators to work with. ...”

(Source: ENDS, 14th december 2011)



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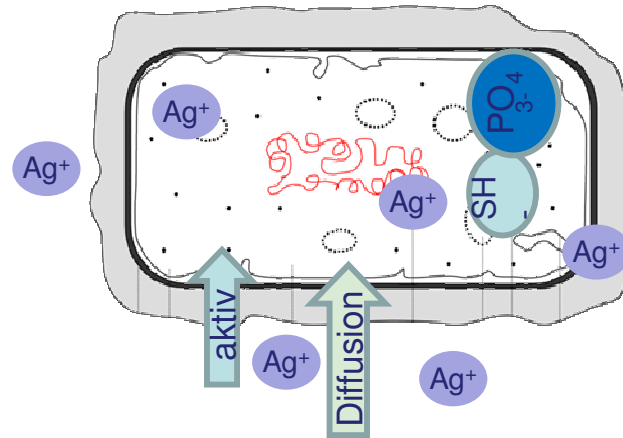
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# Silver as antimicrobial agent



Antimicrobial effect caused by  $Ag^+$

$Ag^+$     $Ag^+$     $Ag^+$     $Ag^+$     $Ag^+$     $Ag^+$



Silver ion exchangers   Silver salts   Elementary silver   Silver composites

Notified active substances

Silver zirconium phosphat	Silver zeolite	Silver glass	Silver – chloride – nitrate	Silver	Silver on $SiO_2$ ; Silver chloride on $TiO_2$
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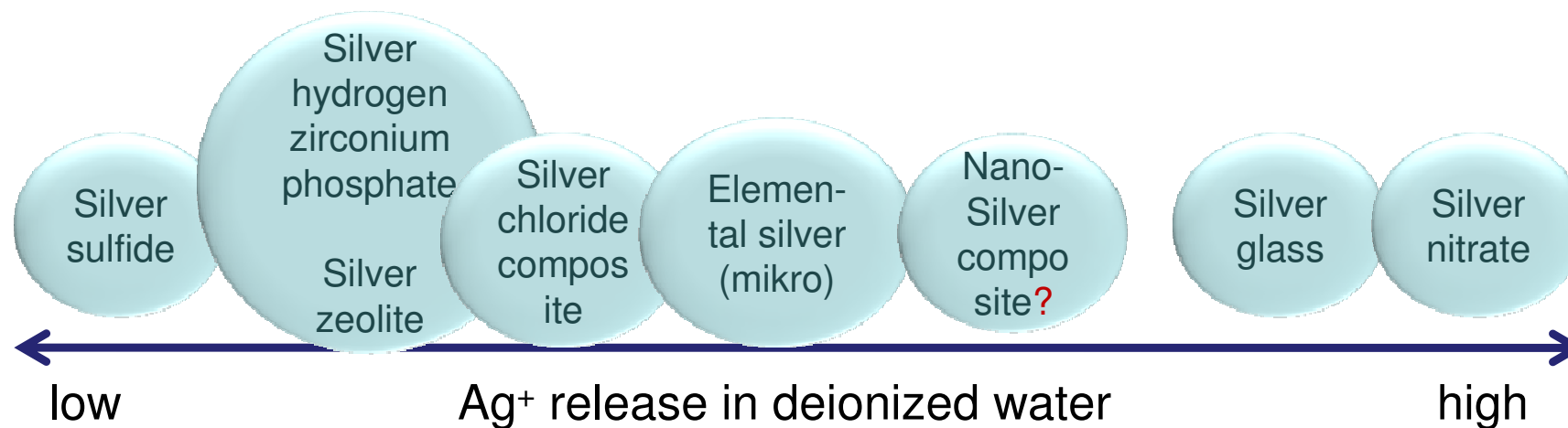
# Silver as antimicrobial agent

Ag<sup>+</sup> release varies over a wide range, dependent on:

- Silver releasing agent
- pH and ion-content of solvent



Nano-silver possibly has a higher release rate per mass of silver due to bigger surface area



# Does size matter?

Example water solubility:

	Silver powder	Nano silver in compound
Particle size	2-55 $\mu\text{m}$	5-20 nm
Water solubility	22.8 mg Ag/L	210.3 mg Ag/L



# Does size matter?

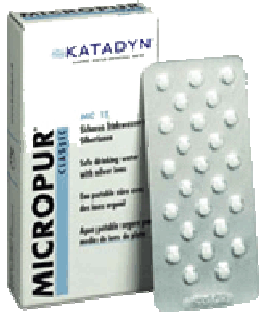


Silver electrode



Powdered silver

# Biocidal applications



www.kemi.se

# Biocidal applications

- **Infinite application(possibilitie)s:**

[http://www.alibaba.com/showroom/germ-free-material\\_3.html](http://www.alibaba.com/showroom/germ-free-material_3.html)

[http://www.housekeepingchannel.com/tag\\_238\\_Antimicrobial](http://www.housekeepingchannel.com/tag_238_Antimicrobial)

<http://www.zoflora.co.uk/>

- **Silver:**

## **The Silver Nanotechnology Commercial Inventory,**

Emma Fauss, University of Virginia, September 2008;

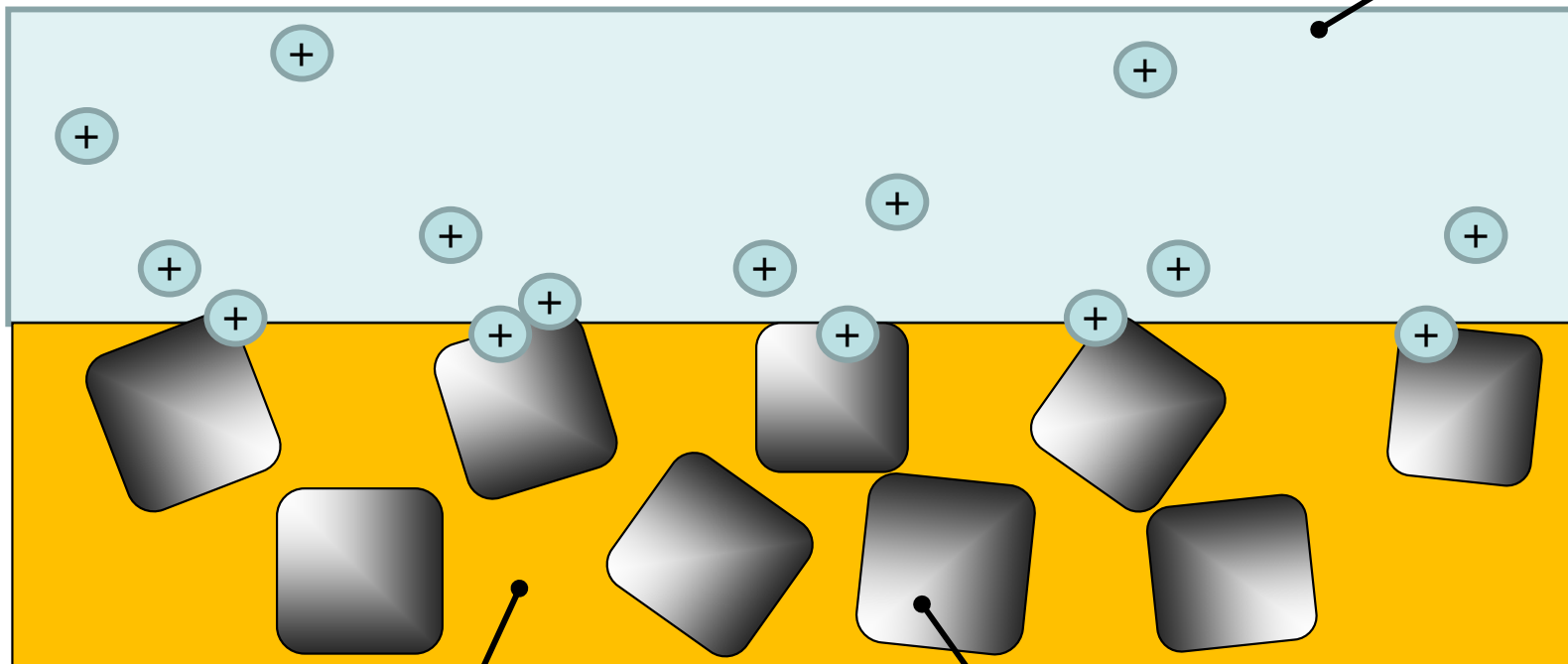
[http://www.nanotechproject.org/process/assets/files/6718/fauss\\_final.pdf](http://www.nanotechproject.org/process/assets/files/6718/fauss_final.pdf)

- products on the market contain real nano-silver, or are named "nano" because that is catchy

# Applications with antimicrobial Silver

Example: Toilet seat

Water film

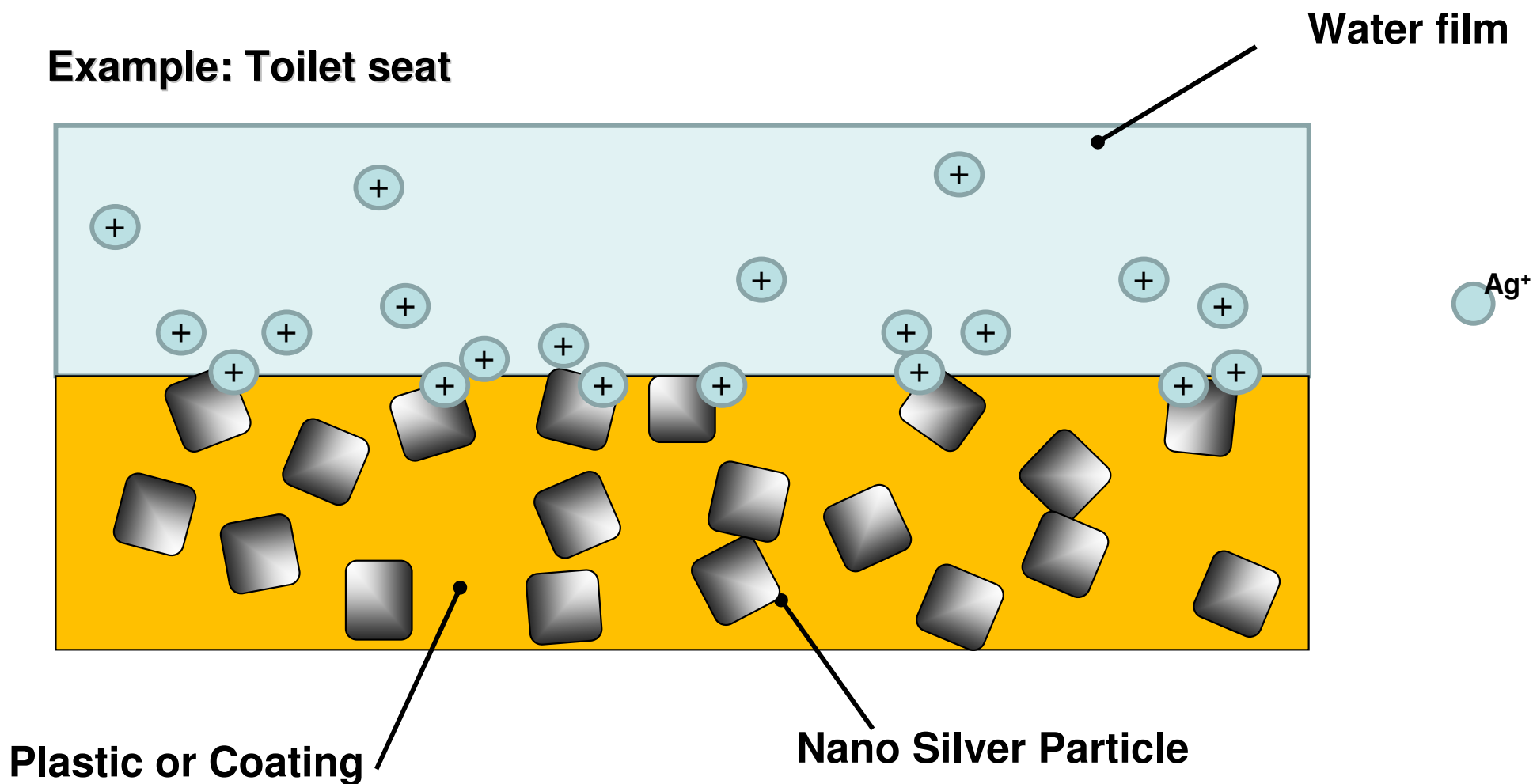


Plastic or Coating

Bulk Silver Particle

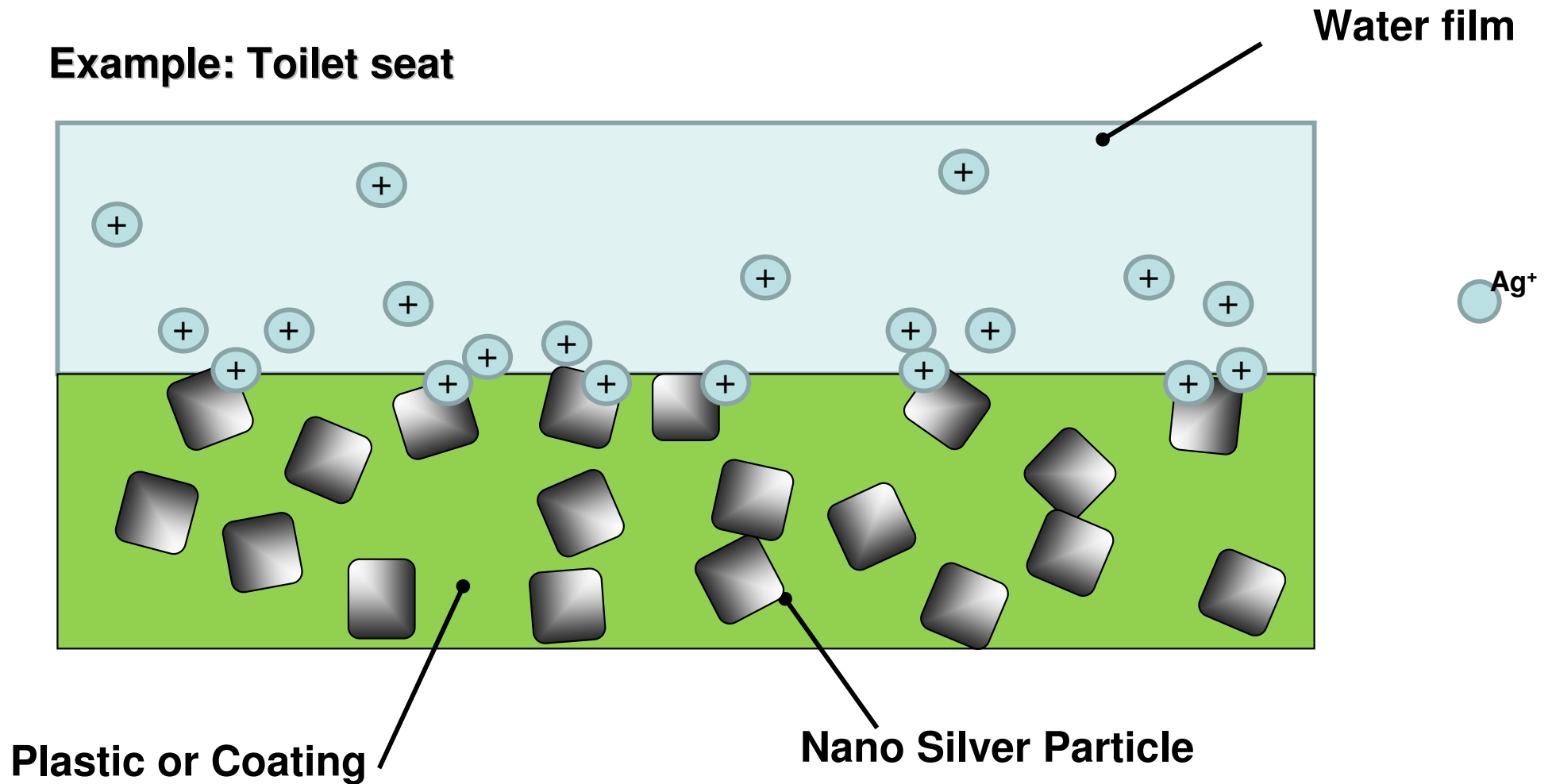
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# Applications with antimicrobial Silver

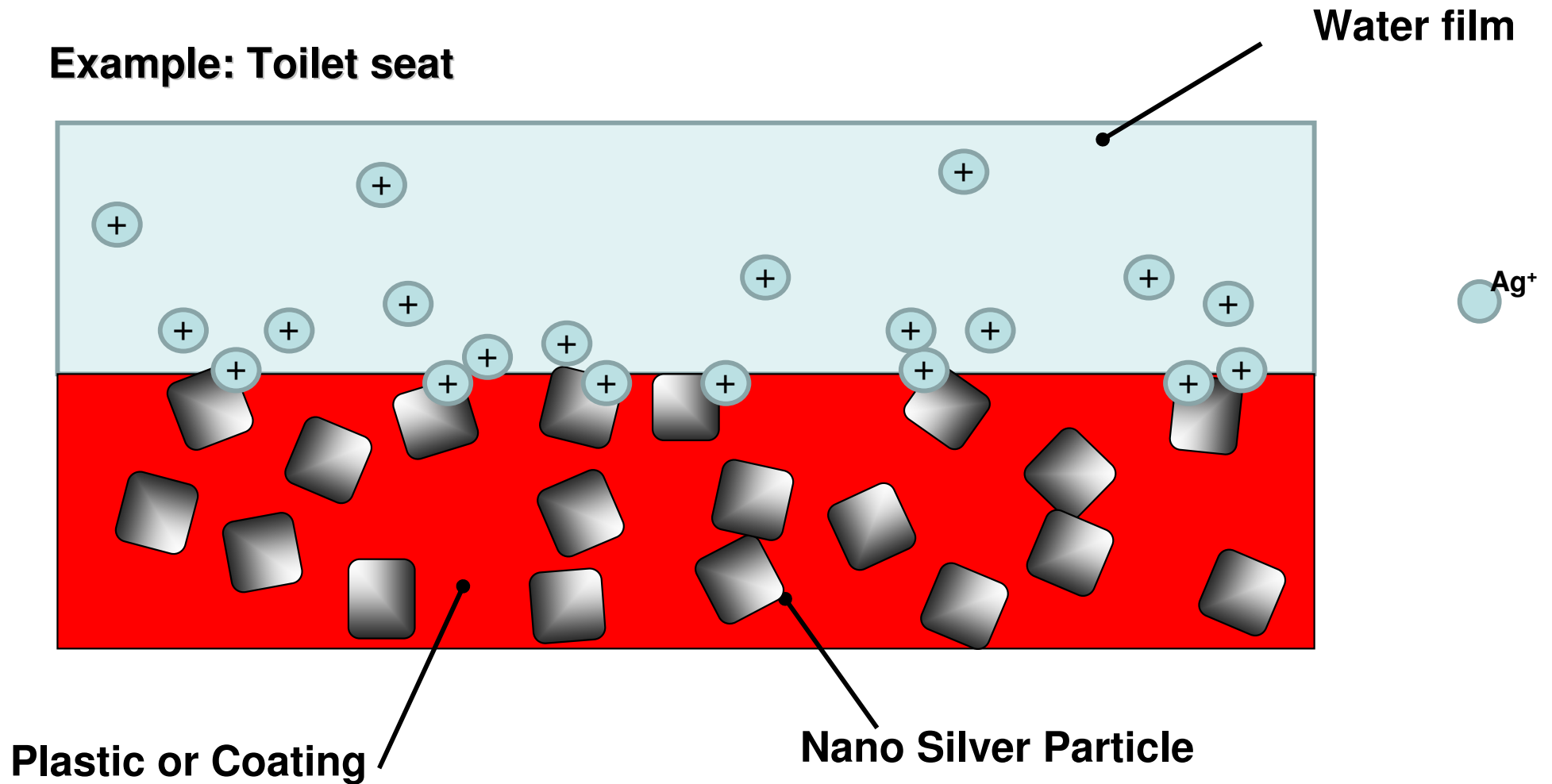
Example: Toilet seat





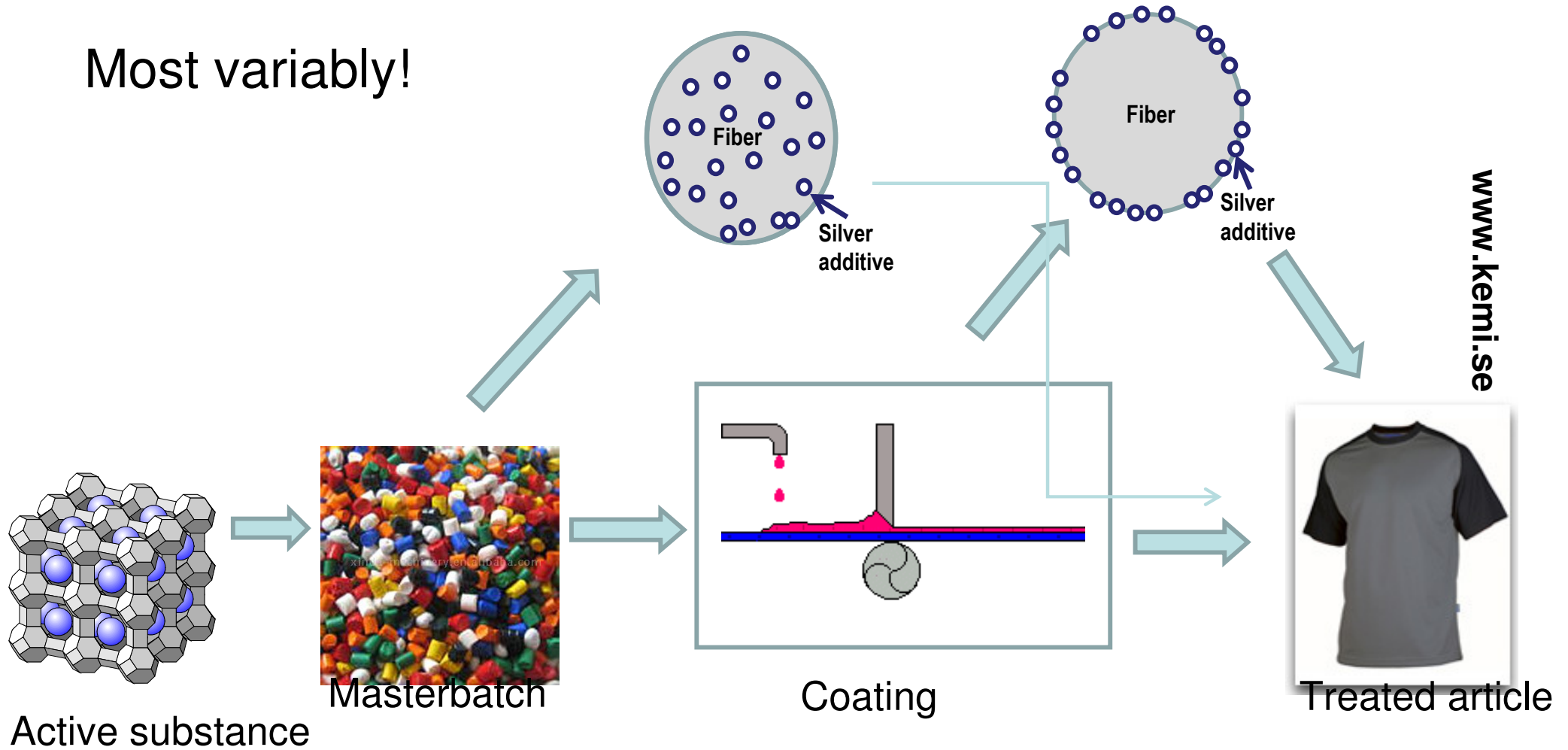
# Applications with antimicrobial Silver

Example: Toilet seat



# How is antimicrobial silver applied?

Most variably!

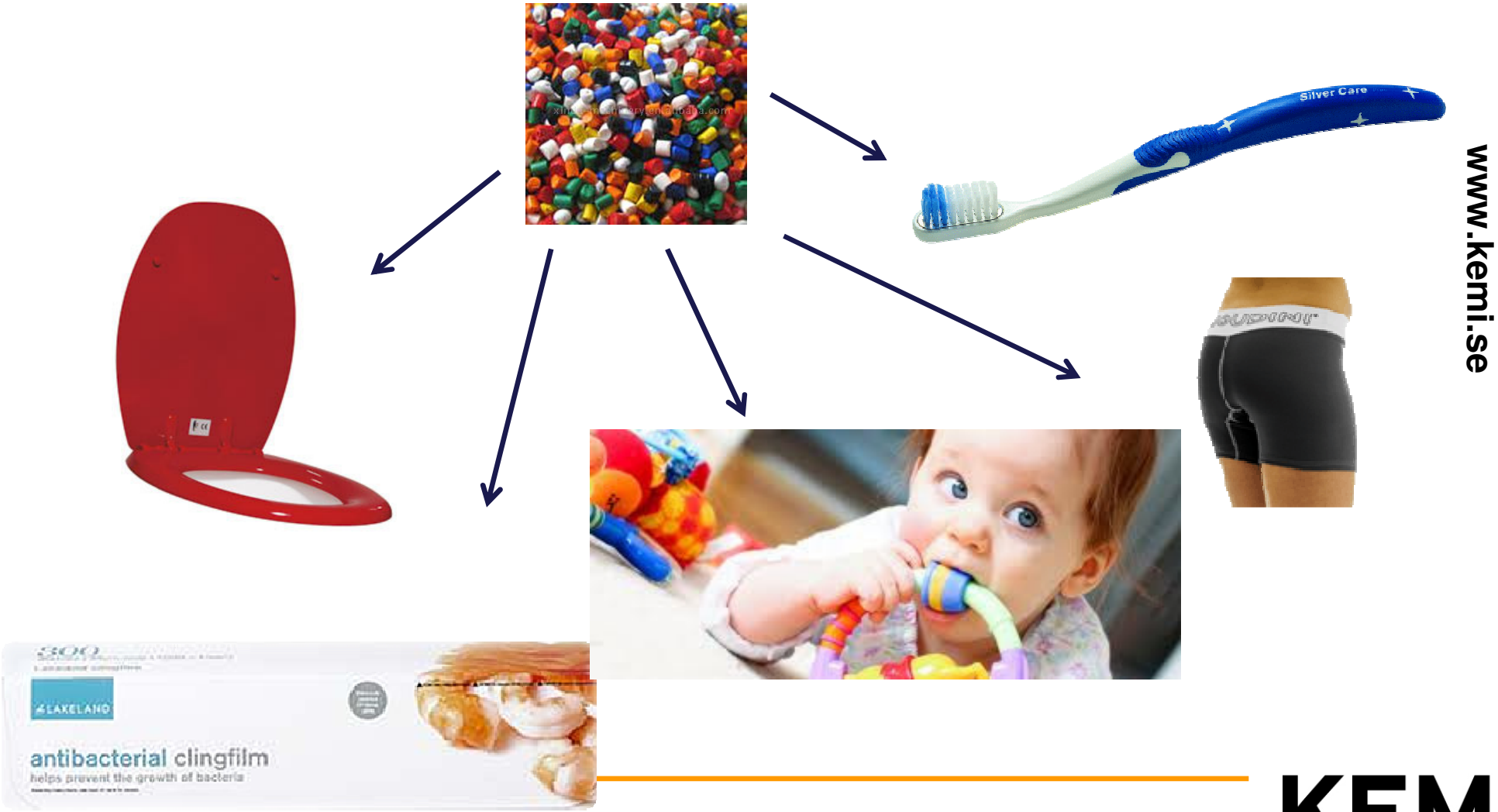


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# Quantity of silver applications

Silver applications	treated article	coating	textile	liquid consumer	liquid industrial
Overall distribution (%)	31	49	10	3	7

# Exposure Assessment



# Exposure Assessment

- Workers exposure → SCAS (including nano)
- Consumer exposure → only Ag<sup>+</sup> ??  
» Abrasion? Coating?
- Environmental exposure → only Ag<sup>+</sup> ??  
» Aggregation? Forming of Nano-Particles?<sup>1)</sup>

- 1) R. D. Glover, J. M. Miller, J.E. Hutchinson: Generation of Metal Nanoparticles from Silver and Copper Objects: Nanoparticle Dynamics on surfaces and Potential Sources of Nanoparticles in the Environment (in publication)  
<http://pubs.acs.org/doi/abs/10.1021/nn2031319>

# New in Biocides Regulation

## Article 4, Conditions for approval

.....

*4. The approval of an active substance shall not cover nanomaterials except where explicitly mentioned.*

This is a result of EP's position during first reading:

**“....Special attention to nanomaterials**

Lastly, with doubts remaining over the possible long-term health effects of nanomaterials, MEPs insisted on the need for separate assessment of such particles in biocidal products” (source: EPs website)

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# New in Biocides Regulation

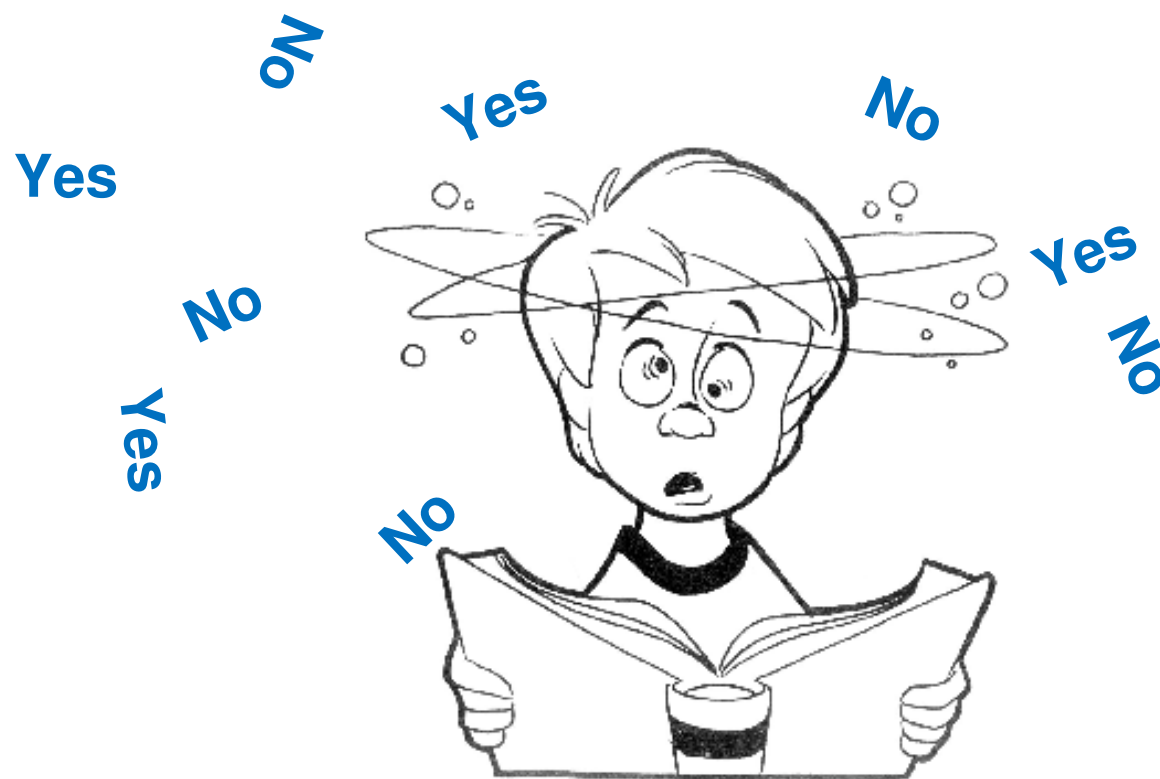
- **Treated articles** are defined (Art. 3 (l))
- Use of a biocidal product includes use in **treated articles** (Art. 3 (k))
- **Articles** may only be placed on the market in Europe when **treated** with biocidal products which contain **active substances authorized in Europe**
- **Treated articles** have to be labelled:
  - *if they make a biocidal claim*
  - *if they contain nanomaterial*
  - *if there is considerable release (decided upon at active substance authorization)*

# Conclusions

- Nano is an issue – amongst others – for the evaluation of silver
- The original active may be in nano-size → the form man and environment are exposed to might be very different
- The focus on "Nano" can obscure the issues which deserve even more attention
- Exposure for different uses and application areas is the biggest challenge in the evaluation of silver

# Conclusions

Nano or not nano. Is that a question?



# Applications with antimicrobial Silver



Spray applications:

Probably high exposure during use

→ Different assessment depending on (end-)use??

# Kemis Washing Study

Scope: 30 different textiles were purchased and analysed for silver before, after 3 x and after 10 x washing

- The original content varied to a large extent. Between 0,4- 1360 mg/kg textile
- In general the original content of silver was between 10-50 mg/kg
- After 10 washes the samples had leached between 10-98 %. In many cases > 80 %
- Already after 3 washes 10 of the samples leached > 43 %

# Different Assessment of Different Silver Forms?

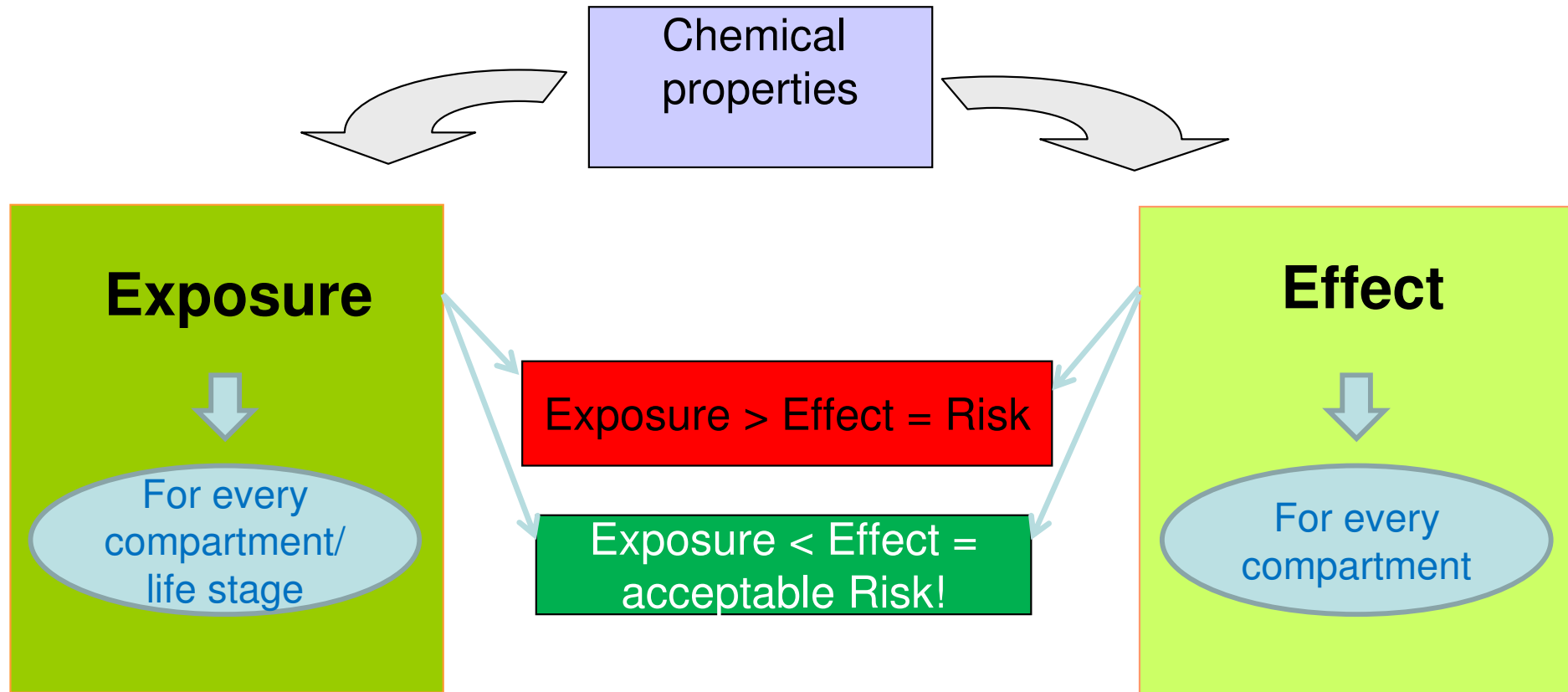
Silver form	Competent Authority Report	Inclusion decision
Silver zinc zeolite	x	x
Silver copper zeolite	x	x
Silver nitrate	x	x
Silver sodium hydrogen zirconium phosphate	x	x
Silver phosphate glass	x	x
Silver borosilicate glass	x	x
Silver (electrode, powder)	x	x x
Silver chloride on TiO <sub>2</sub>	x	x
Silver nano-composite	x	x

# Risk Assessment

## Risk: Hazard x Exposure

- Hazard:  
inherent properties of a substance  
→ Tox studies with representative organisms
- Exposure:  
For every compartment and life stage  
→ Model calculations

# Risk Assessment



Risk characterisation – compartment, life stage