# Formaldehyde releasers: principles of chemistry and hydrolysis

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# Formaldehyde and Formaldehyde releasers in BPD/BPR

Formaldehyde supported for:

- PT2 (Private area and Public Health Area Disinfectant) –surface disinfection in hospitals
- PT3 (Veterinary Hygiene Biocidal Products)
- PT20 (Preservatives for Food or Feedstocks)
- PT22 (Embalming and taxidermist fluid) – embalming only

Formaldehyde-Releasers supported for *:

- PT2 (Private area and Public Health Area Disinfectant and other Biocidal Products )
- PT6 (In-can Preservatives)
- PT11 (Preservative for Liquid Cooling and Processing Systems)
- PT12 (Use as Slimicide )
- PT13 (Preservative in Metal Working Fluids )

* probably not comprehensive

# Formaldehyde releaser in BPD/BPR

FAR represent a larger group of chemicals supported for different product types; main application area is PT6 and PT13

| Name | CAS | PT 2 | PT 6 | PT 11 | PT 12 | PT 13 |
|---|---|---|---|---|---|---|
| Reaction products EGForm | 3586-55-8 | X | X | X | X | X |
| HHT | 4719-04-4 | | X | X | X | X |
| MBM | 5625-90-1 | | X | | | X |
| DMDMH | 6440-58-0 | | X | | | X |
| Oxazolidin/MBO | 66204-44-2 | X | X | X | X | X |
| CTAC | 4080-31-3 | | X | | X | X |
| Cis CTAC | 51229-78-8 | | X | | | X |
| TMAD | 5395-50-6 | X | X | X | X | X |
| EDHO | 7747-35-5 | | X | | | X |
| (benzyloxy)methanol | 14548-60-8 | | X | | | X |
| HPT | 25254-50-6 | X | X | X | | X |
| Sodium N-(hydroxymethyl) glycinate | 70161-44-3 | | X | | | |

# General principles for formaldehyde releasers

- Formaldehyde Releasers (FAR) are supposed to be “carrier systems” or “transport systems” for formaldehyde
- They are intended/designed to release formaldehyde under use conditions
- FAR itself are concentrates which are supposed to be stable and do not decompose unless they are diluted with water.
- In aqueous dilutions however formaldehyde is released and this release follows individual kinetics depending on several factors such as the type of releaser and the binding strength of formaldehyde

# Formaldehyde releasers:
# What is common where are the differences?

Common properties

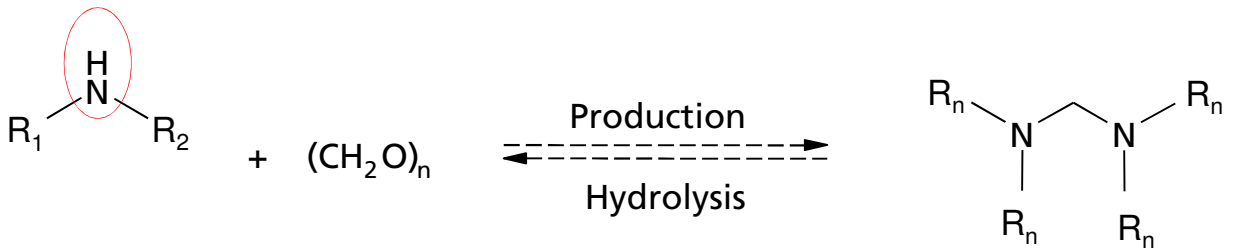
- hydrolytic instability
- release of a pre-defined amount of formaldehyde
- an equilibrium between reactants and product
- Complete hydrolysis at high dilutions in water (approx < 0.1%)

Differences

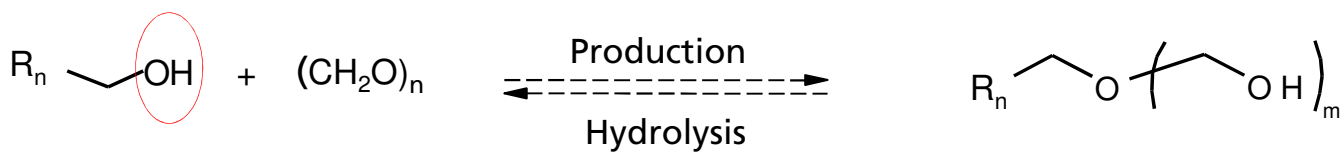
- chemical identity (i.e. O-formal and N-formal)
- composition (single substance or reaction mixture)
- binding strength of formaldehyde and the degree of dilution in water required for hydrolysis, pH dependency of hydrolysis
- presence of by-products
- amount of max releasable formaldehyde (10% -50%)

# General structure of formaldehyde releasers

## N-formal

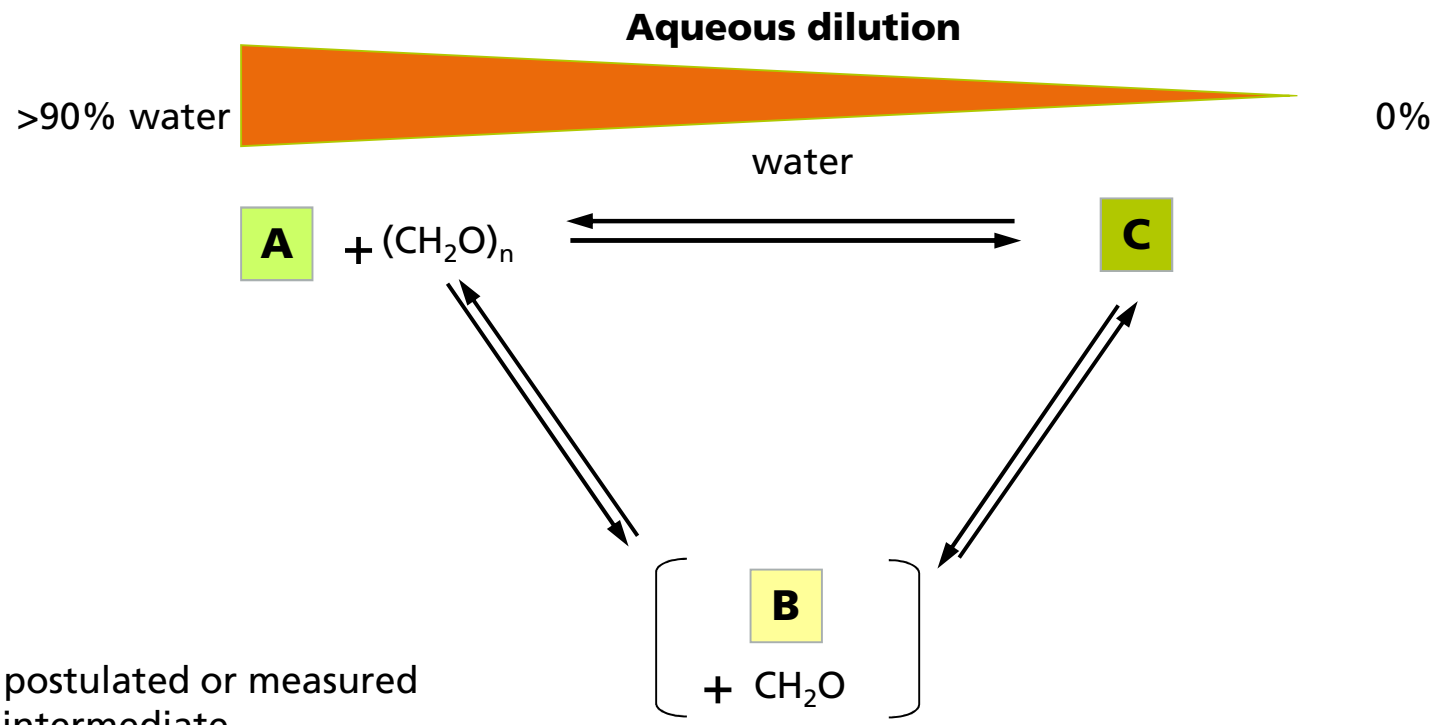



## O-formal



# Formaldehyde release – scheme for equilibrium reactions

The basic principle is a release of formaldehyde only in the application phase

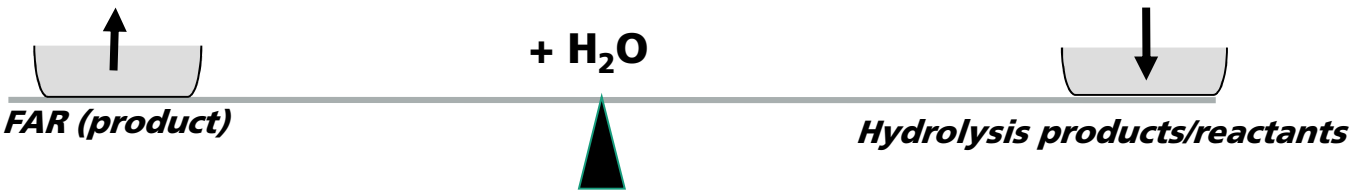


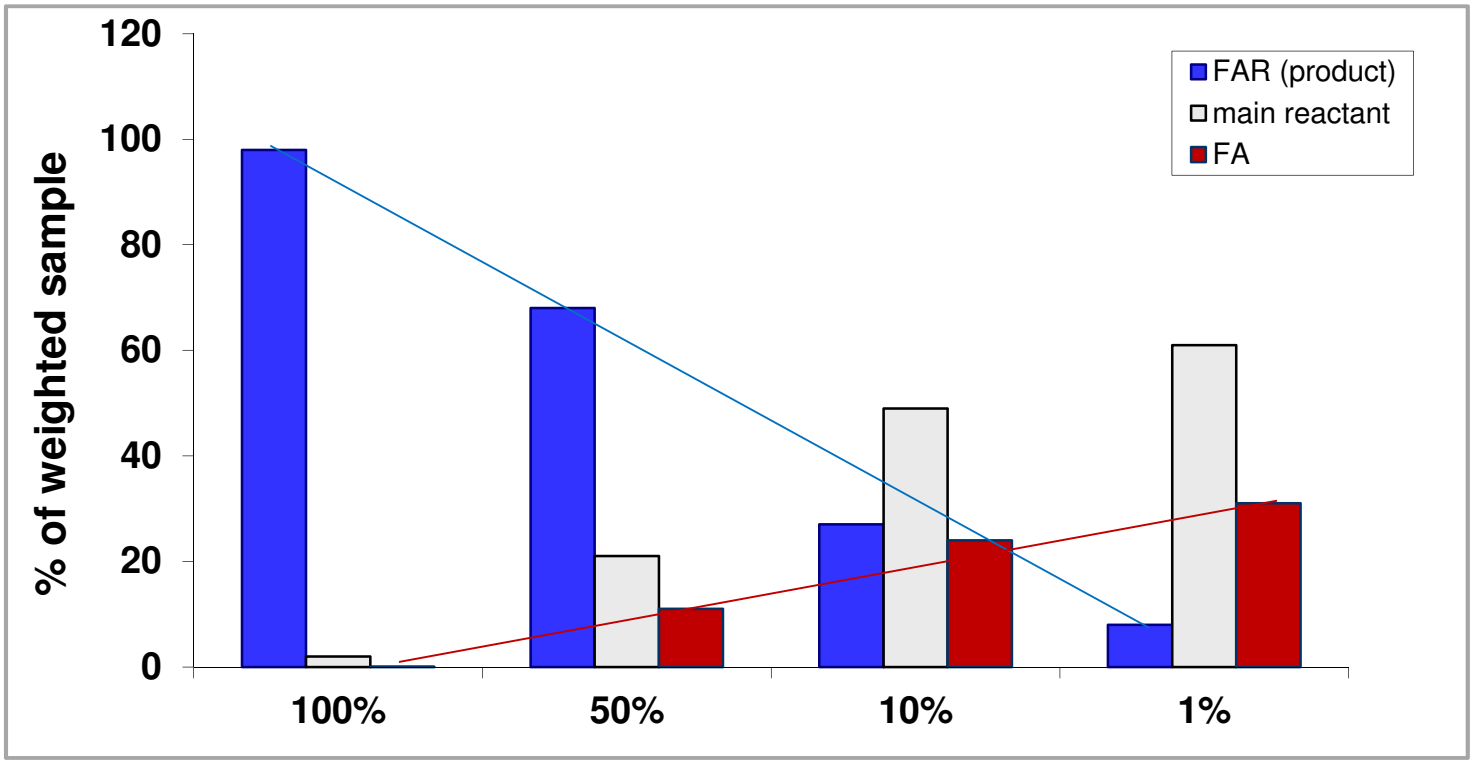

**B** = postulated or measured intermediate

**A** = single substance or,
= two or more reactants/hydrolysis products

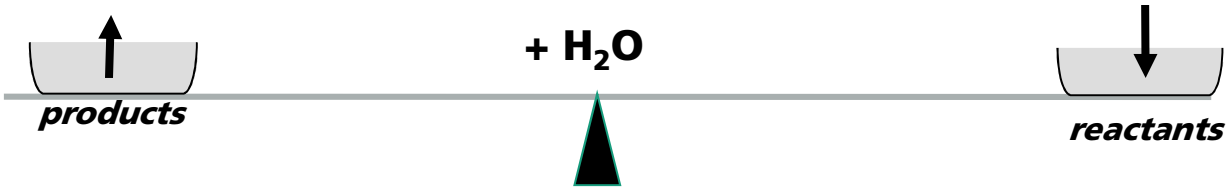
**C** = single substance or,
= two or more substances in equilibrium,
= complex reaction mixture including oligomeric structures

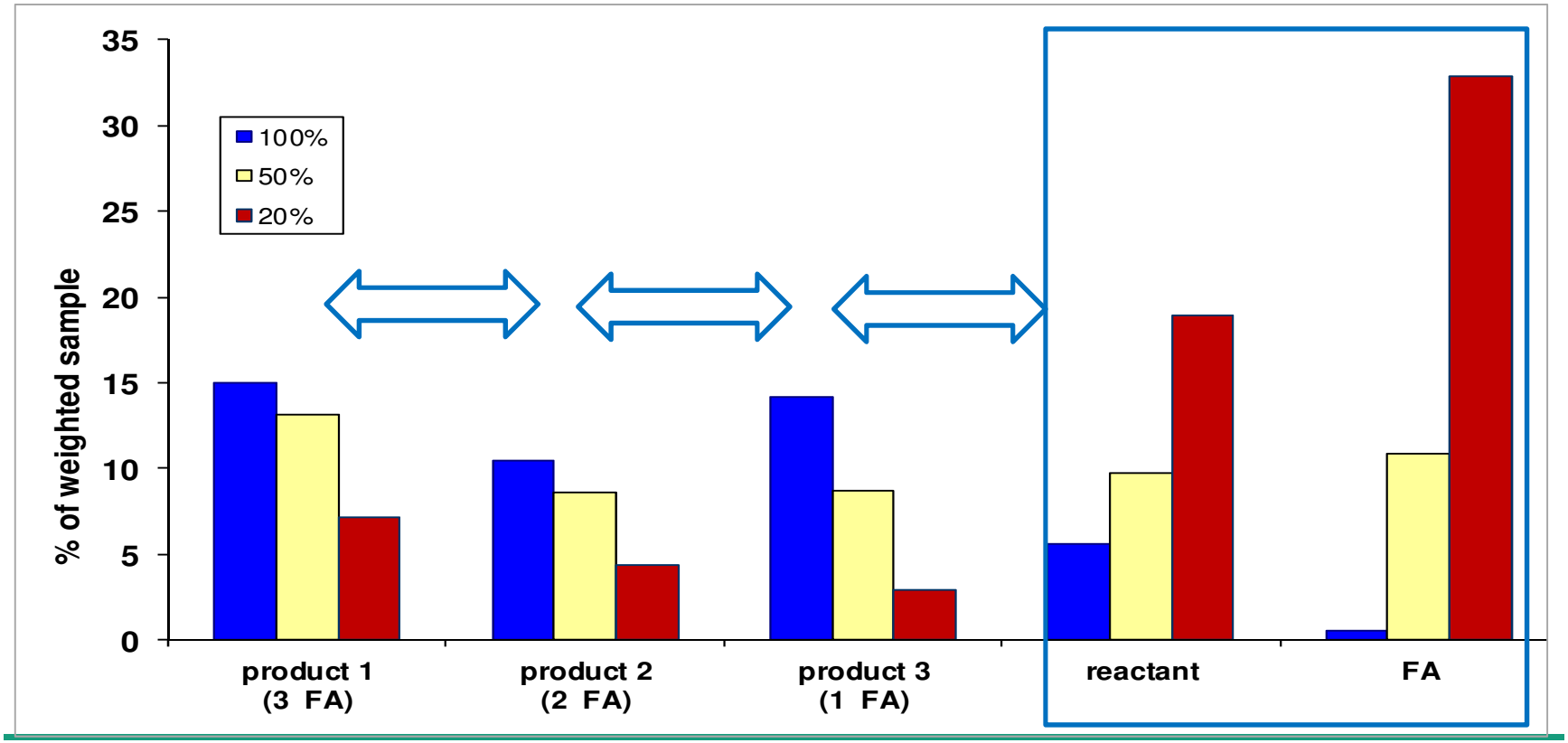
# Hydrolysis/formaldehyde release: dilution dependency



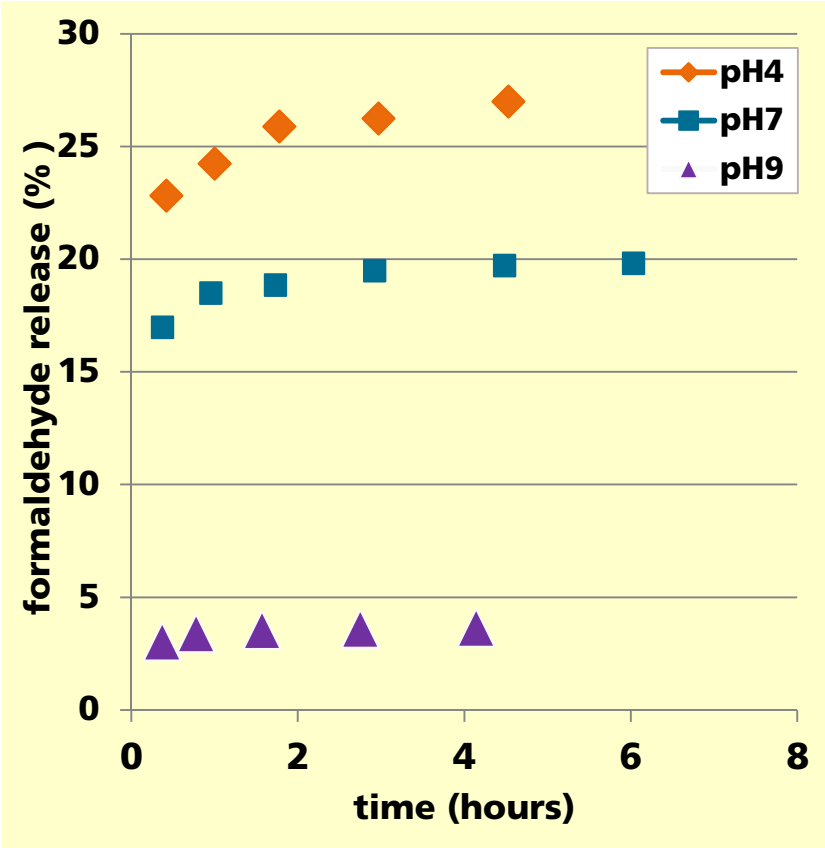
# Hydrolysis/formaldehyde release: complex system



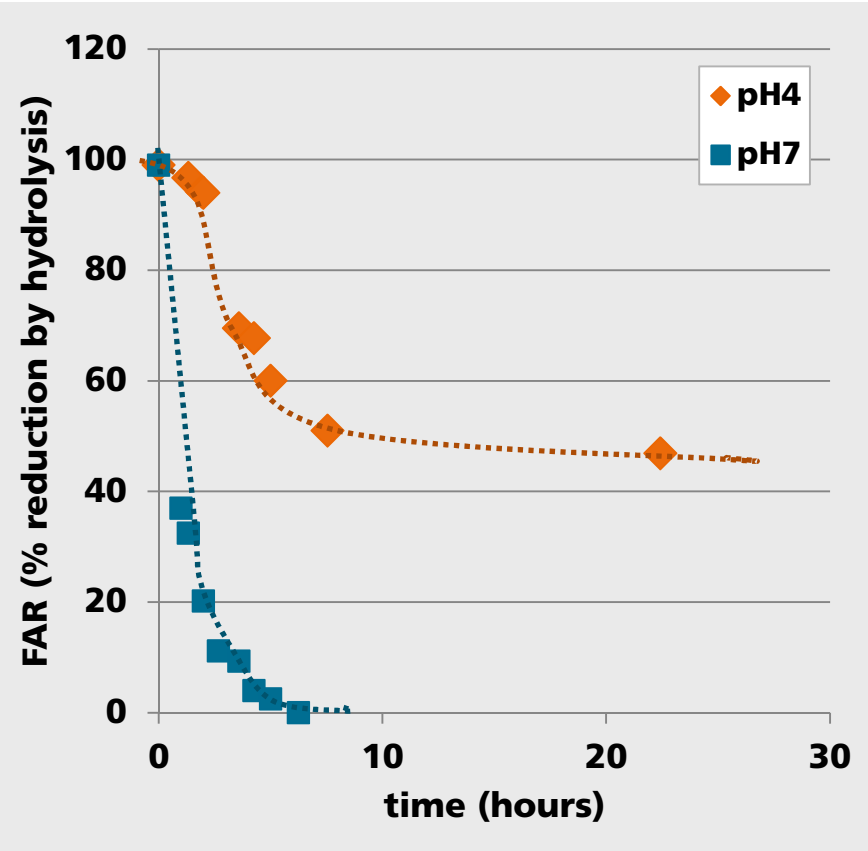
# Hydrolysis/formaldehyde release: pH dependency

Example A



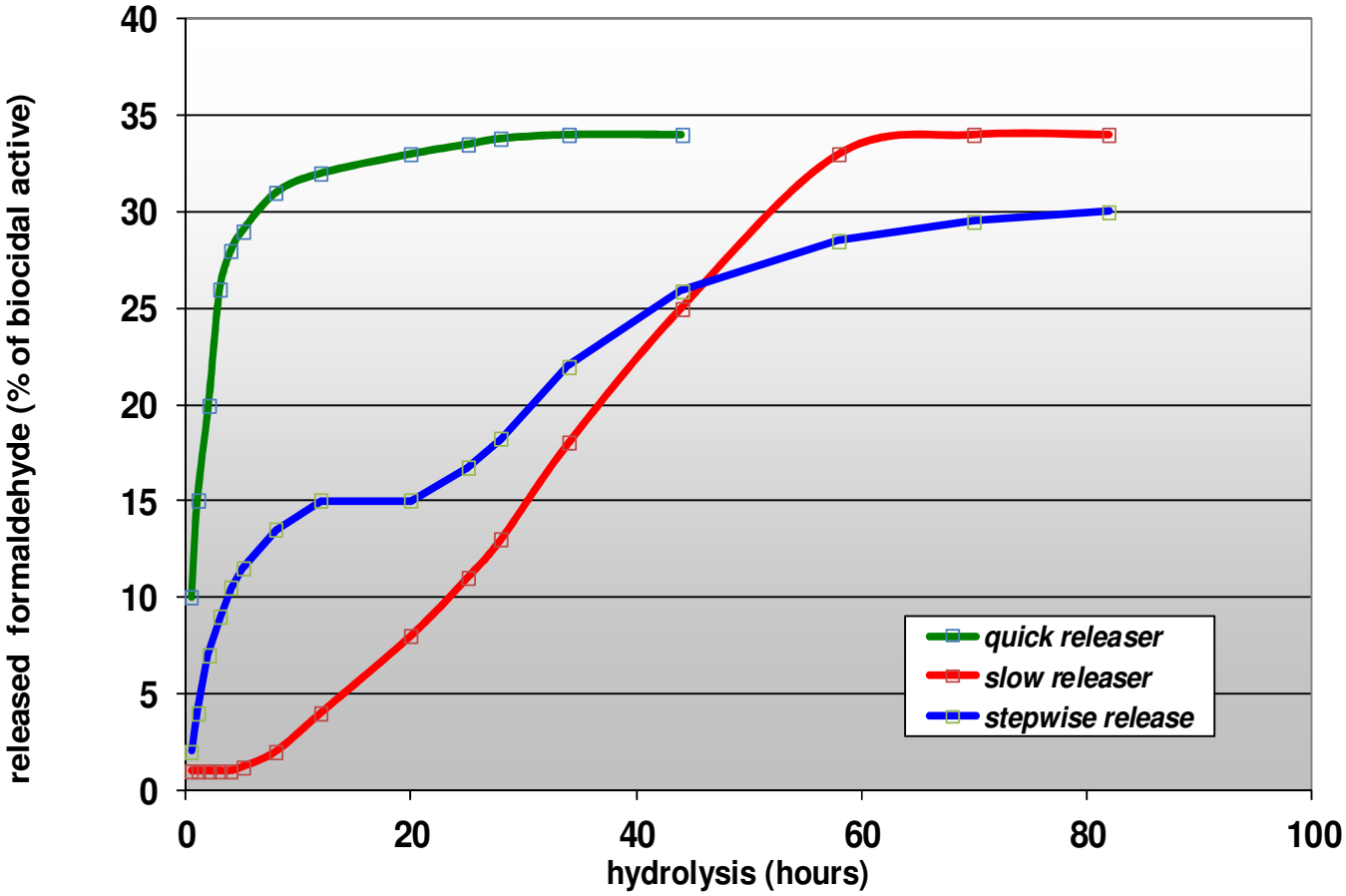

rapid hydrolysis at pH 4

Example B




at pH 4 more stable than at pH7

# Kinetic of hydrolysis: differentiation of releaser types



# Problems/challenges for the biocidal dossier: Identity

- FAR as a single substance or defined multi component substance
  *the identity is clear but*
  *-- a „non-invasive“ analytical method is required for purity and impurities*
- FAR as reaction product ⇉ UVCB
  *the identity is defined by the production process and*
  *-- a „non-invasive“ analytical method is required for constituents*

- Which is the active substance? (□ in situ discussion)
  *how will the Annex/List entry look like?*
  *what are the data requirements – for which substance?*
  *what is relevant for classification and labelling?*

- What kind of analytical method is required?
  *monitoring of production and formulation of biocidal products*
  *monitoring of human and environment*

# FAR in the in-situ discussion

## Methods for the in-situ generation of biocidal active substances

- Chemical reaction
  (Tetraacetylethylenediamine (TAED) …. generating peracetic acid)
- Electrolysis and electrical generation
  (Sodium chlorite generating chlorine dioxide via electrolysis)
- Hydrolysis to form an acid-base pair
  (Substituted hydantoins hydrolysing to hypohalous species)

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**ENV.D.3 - Chemicals, Biocides and Nanomaterials**

**CA-May12-Doc.6.2a**
**Final post CA**

**GUIDANCE NOTE ENDORSED BY COMPETENT AUTHORITIES FOR BIOCIDAL PRODUCTS**

*This document is an attempt to provide guidance in the interest of consistency, and has been drafted by the Commission services responsible for biocidal products with the aim of finding an agreement with all or a majority of the Member States' Competent Authorities for biocidal products. Please note, however, that neither the Commission, nor Member States are legally obliged to follow the approach set out in this document, since only the Court of Justice of the European Union can give authoritative interpretations on the contents of Union law.*

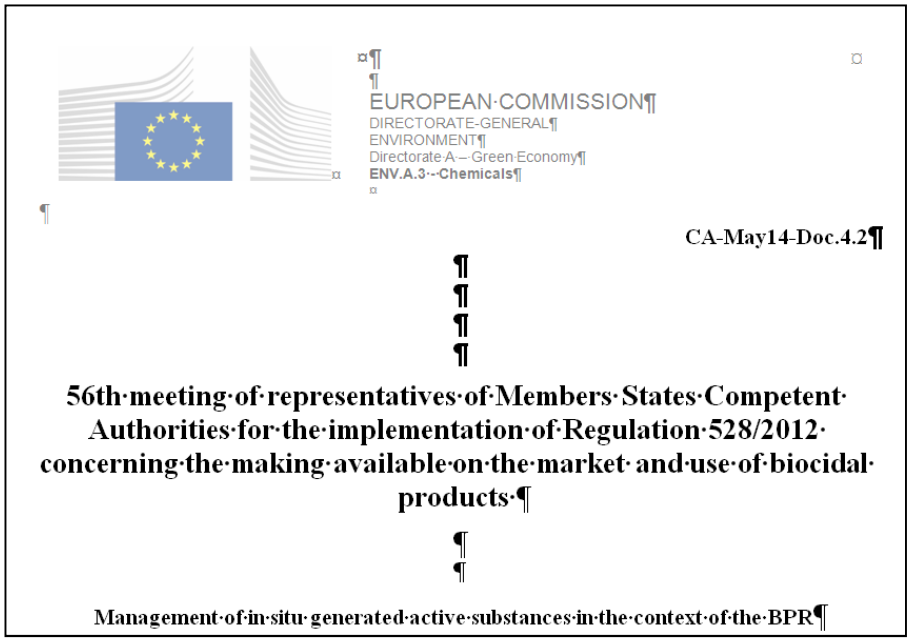
**Governance under the Biocidal Products Directive of active substances generated in situ**

- Formation of the in-situ generated active substance during use
  (Various substances releasing formaldehyde)

# In-situ (2)

31 January 2014 "*Call for information on in-situ generated biocidal active substances*" the call was released by the European Commission companies were invited to submit information by 31 March 2014.

14 suspected FAR are listed here (including paraformaldehyde)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CA-May14-Doc.4.2

56th meeting of representatives of Members States Competent Authorities for the implementation of Regulation 528/2012 concerning the making available on the market and use of biocidal products

Management of in situ generated active substances in the context of the BPR

The Commission therefore proposes that under the BPR the eventual approval of an active substance, which can be generated in situ, shall not refer to the precursors used for the generation of the active substance, when more than a single combination of precursors can be used to generate the active substance.

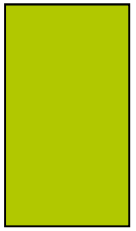
This shall however not apply to active substance releasers, such as formaldehyde releasers, which shall continue to be listed in accordance with the practice developed under the BPD

# Problems/challenges for the biocidal dossier: Exposure

Life cycle of the biocidal active substance:
which substances are present at different life cycle steps

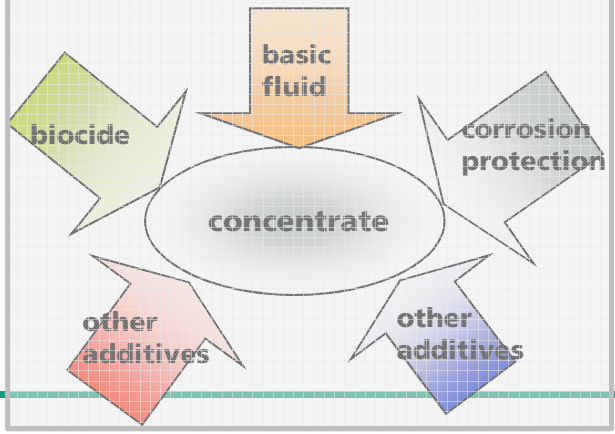
***production of biocidal active substance***

concentration of a.s.100%



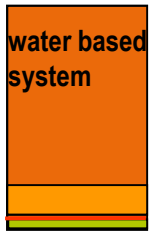
***formulation of concentrates***

concentration of a.s. 2-3%




***use of biocidal active substance***

concentration of a.s. 0.1-0.15%



# Problems/challenges for the biocidal dossier: Exposure

Which substances are present at different life cycle steps:
basic assumptions for FAR

| | ***production*** Concentration:100% | ***formulation concentrate*** concentration: 2-3% | ***use in metal working*** Concentration: 0.1-0.15% |
|---|---|---|---|
| **exposure to** | **a.s. (100%)** | **a.s. (100%) and concentrate (2-3%)** | **Due to high dilution (degradation products: reactant & formaldehyde)** |
| **route(s) of exposure** | dermal, inhalation | dermal, inhalation | dermal, inhalation |
| **emission into** | **water via STP** | **water via STP** | **use: water via STP recycling: water via STP** |

# Problems/challenges for the biocidal dossier: Study design

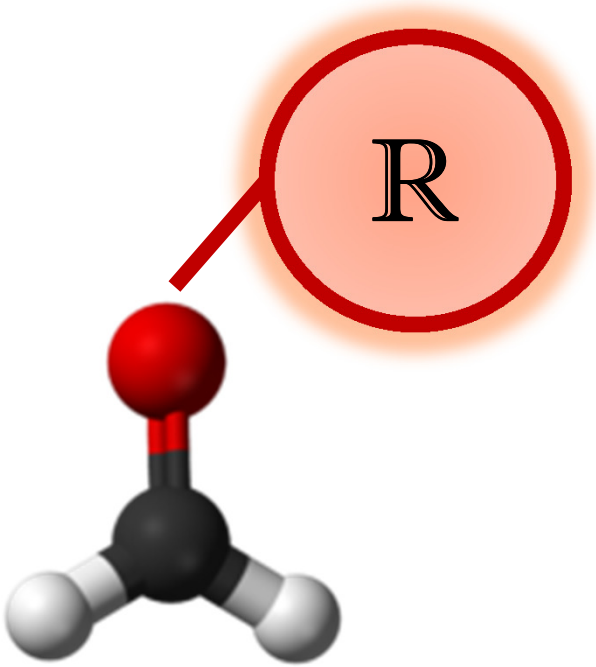
- Many test systems/guideline studies use applications in aqueous dilutions

  especially for ecotoxicity and genotoxicity testing the hydrolysis products are tested

- All studies need a careful consideration what is tested and what should be tested

# Summary

- Formaldehyde Releasers (FAR) are chemicals that are grouped mainly by their property to release formaldehyde under use conditions
- They might differ considerably in their release kinetics, the amount of maximal releasable formaldehyde and the binding strength for formaldehyde
- A detailed knowledge about the FAR is required for a risk assessment
- There are several problems in testing and assessment which are common for all FAR



Thank you very much for your attention